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Chemical Kinetic and Photochemical Data for Use in Stratospheric Modelling

Evaluation Number 4:
NASA Panel for Data Evaluation

January 15, 1981

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ABSTRACT

This is the fourth in a series of evaluated sets of rate constants and photochemical cross sections compiled by the NASA Panel for Data Evaluation. The primary application of the data is in the modelling of stratospheric processes, with particular emphasis on the ozone layer and its possible perturbation by anthropogenic and natural phenomena.

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CHEMICAL KINETICS AND PHOTOCHEMICAL DATA

FOR USE IN STRATOSPHERIC MODELLING

INTRODUCTION

The present compilation of kinetic and photochemical data represents

the fourth evaluation prepared by the NASA Panel for Data Evaluation. The

Panel was established in 1977 by the NASA Upper Atmosphere Research Program

Office for the purpose of providing a critical tabulation of the latest

kinetic and photochemical data for the use by modellers in computer simula-

tions of stratospheric chemistry. The previous three publications appeared

as follows:

Evaluation Number	Reference
1	NASA RP 1010, Chapter 1 (Hudson, 1977)
2	JPL Publication 79-27 (DeMore et al., 1979)
3	NASA RP 1049, Chapter 1 (Hudson and Reed, 1979)

The present composition of the Panel and the major responsibilities of each member are listed below:

W. B. DeMore, Chairman (Chapman chemistry)

L. J. Stief, Vice-Chairman (methane oxidation, sulfur chemistry)

F. Kaufman, Advisor

D. M. Golden (three-body reactions)

R. F. Hampson (NO_x chemistry, $O(^1D)$ reactions)

M. J. Kurylo (NO_x, SO_x chemistry, $O(^1D)$ reactions)

J. J. Margitan (HO_x chemistry)

M. J. Molina (photochemical cross sections)

R. T. Watson (halogen chemistry)

As shown above, each Panel member concentrates his effort on a given area or type of data. Nevertheless, the final recommendations of the Panel represent a consensus evaluation by the entire Panel. Each member reviews the basis for all recommendations, and is cognizant of the final decision in every case.

BASIS OF THE RECOMMENDATIONS

The recommended rate constants and cross sections are based on laboratory measurements, and in general only published data are considered. Occasional exceptions are made when preprints of articles submitted for publications are available to the Panel. In no cases are rate constants adjusted to fit observations of stratospheric concentrations. The Panel does consider the question of consistency of data with expectations based on kinetics theory, and in cases where a discrepancy appears to exist, this fact is pointed out in the accom-

panying note for each entry. The major use of theoretical extrapolation of data is in connection with three-body reactions, in which the required pressure dependence is sometimes unavailable from laboratory measurements, and can be estimated by use of appropriate theoretical treatment. In the case of a few important rate constants for which no experimental data are available (for example, $OH + HOCl \rightarrow H_2O + ClO$), the Panel has provided estimates of rate constant parameters, based on analogy to similar reactions for which data are available.

The Panel takes a conservative approach to changing recommendations. It is felt that it is preferable to continue a recommendation that may be incorrect than to change to one that may also be incorrect. Thus, changes are not made unless there is strong evidence that the new recommendation is more reliable. The objective of this approach is to avoid erratic changes which would lead to great confusion in the model predictions. Of course, when there is evidence that a given recommendation has been placed in doubt by new work, that fact is very clearly pointed out in the note accompanying that entry. In the present evaluation the Panel was faced with several situations in which important rate constants were subject to possible revision based on new evidence. (These are discussed in detail in the notes.) In some cases, however, no change was made because it was felt by the majority of Panel members that the situation was not sufficiently clear to warrant a new recommendation at this time.

DISCUSSION

Status of Stratospheric Chemistry

Inadequacies in rate constant data still constitute a major source of uncertainty in stratospheric chemistry. Although it seems unlikely that our

present concept of stratospheric chemistry will change in a qualitative way, it is possible that quantitative changes will occur which may modify current predictions (e.g., the extent of O_3 depletion by CFMs) to a significant degree. This is not to suggest that current hypotheses such as the Rowland-Molina formulation of stratospheric chlorine chemistry are likely to be disproven; rather, the intention is to indicate that further refinements are possible.

The major problems encountered by the Panel in the present evaluation tend to fall in the following categories:

1. Inexplicable disagreements among different experimental studies.

2. Lack of information on reaction mechanism and products.

3. Reports of unexplainable temperature dependences and/or A-factors.

Category 1 was a problem in the case of the $OH + HO_2$ reaction. In this case, low pressure flow discharge results (Chang and Kaufman, 1978) seem to be compatible only with $k < 5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, whereas several other studies, under higher pressure conditions, point to $k \geqslant 1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. (DeMore and Tschuikow-Roux, 1974; Hochanadel et al., 1974 and 1980; Lii et al., 1980a). The reason for this discrepancy is not known, and this problem illustrates the need for definitive studies over a wide range of reaction conditions. In view of the great uncertainty surrounding this important reaction, the Panel has decided not to change from the previous recommendation of $k = 4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, despite the newer evidence in support of a higher value.

Kinetics measurements usually are based on the rate of disappearance of reactant(s), rather than on rate of product formation. In most cases the identity of the product is known with certainty, and in such cases there is no

difficulty with this approach. In a few significant reactions, however, more than one product or reaction branch is possible, and there is not necessarily a one-to-one correspondence between reactant disappearance and formation of a given product. An important example of this ambiguity is the chlorine nitrate reaction. The rate of ClO disappearance in the presence of NO_2 has been reliably measured by several groups, but it is not certain that the product is stable chlorine nitrate, rather than a mixture of isomers. (See reaction notes for further details of this problem.)

Other important reactions in which the products are not known with certainty are $OH + HO_2NO_2$, $OH + HNO_3$, $ClO + HO_2$, and $OH + ClO$. Some of these uncertainties can materially affect the model calculations.

Occasionally, laboratory measurements have yielded results which seem to be inconsistent with expectations based on theory or past experience with similar reactions. An example is the $HO_2 + O_3$ reaction, which has a reported A-factor much lower than that expected on the basis of transition state theory. Nevertheless, the experimental measurement appears to be reliable, and, moreover, the reported rate constant can be independently derived with good agreement from ratio measurements involving that reaction and the $HO_2 + HO_2$ reaction. There is no choice, therefore, but to recommend the experimental result, despite the seeming incompatibility with theory. Even so, such discrepancies must ultimately be explained either by a refinement in the theory or by an increased understanding of the nature of the reaction. In the past, disagreement with theory has often been a warning that the experimental measurement was incorrect. An example of this has recently come to light; i.e., the previously recommended rate constant for the $OH + H_2O_2$ reaction, based on experimental measurements, involved an A-factor of 1×10^{-11}. It was recog-

nized by the Panel that this was higher than expected for an OH abstraction reaction, and indeed recent measurements now indicate that the true A-factor is lower, falling in the expected range of about 3×10^{-12} cm^3 s^{-1}.

A somewhat related problem exists with regard to unusual temperature and/ or pressure dependences shown by several reactions, such as HO_2 + ClO, HO_2 + HO_2, OH + CO, and OH + HNO_3. The T-dependences of most reactions over small ranges such as those relevant to the stratosphere can be described adequately by a simple Arrhenius expression. In general, the magnitude and sign of the temperature dependence are understandable in terms of the nature of the reaction; i.e., abstraction reactions involving the breaking of a strong bond have a positive temperature coefficient, whereas association reactions involving free radicals typically have a small negative temperature coefficient. Similar generalizations hold for other reaction types. However, several disturbing exceptions to these behavior patterns have come to light. The HO_2 + ClO reaction (Stimpfle et al., 1979) shows a strong negative dependence below room temperature, but with marked curvature in the Arrhenius plot above room temperature. This behavior implies a more complex reaction mechanism than that described by a single reaction path. This could be very significant, because it is possible that the products change if the reaction path changes, and a small fraction of HCl production (as opposed to the expected products HOCl + O_2) could strongly affect model calculations.

The HO_2 + HO_2 reaction (which in many respects is analogous to ClO + HO_2) shows a similarly strong negative temperature coefficient, although there is no reported evidence of curvature. However, the reaction appears to show a pressure dependence (Thrush and Wilkinson, 1979) which is not expected for a simple atom transfer reaction between two radicals. This again raises the

possibility that the reaction path is more complex than that corresponding to the simple formation of $H_2O_2 + O_2$.

The OH + HNO_3 reaction, which should show a small positive temperature dependence, is in fact reported (Wine et al., 1980a) to have a negative temperature dependence. If correct, this raises the possibility that the reaction proceeds not by abstraction, but rather by addition of OH to HNO_3. At the present time this is of course entirely speculative.

The OH + CO reaction is now well known for a curious and previously unexpected pressure dependence, which is in turn dependent on the presence of O_2. Although the rate constant now appears to be sufficiently well known in an empirical sense, the detailed mechanism needs further elucidation.

All of the foregoing problems illustrate a general need for development of more advanced capabilities in the following areas:

1. Identification of reaction products, especially short-lived ones.
2. Methods to study the chemical and physical properties of unstable or short-lived products.
3. Techniques to study reaction rates under broad ranges of conditions of temperature, pressure, and mixture composition.

In the following sections a few additional points are discussed for the individual reaction categories.

Chapman Chemistry

This class of reactions is relatively well-defined. Two recent studies of the $O + O_2 + M$ reaction, with special attention to the temperature dependence (Klais et al., 1980; Lin and Leu, 1981), have greatly improved the

data base for this reaction, which formerly relied largely on a single measure-
ment. The results of the new work are in substantial agreement with the earlier
work. In connection with the photochemical aspects of Chapman chemistry, there
is some uncertainty about the $O(^1D)$ quantum yields, and some additional work is
required.

No individual recommendations are given for reactions involving O_3 and
$O_2(^1\Delta)$ in their excited vibrational levels. Results from several laboratories
(Kurylo et al. (1974), Rosen and Cool (1975), Gordon and Line (1976)) have
yielded deactivation rate constants for $O_3(v > 0)$ by N_2, O_2 and H_2O which are
of such a magnitude as to preclude its reactive involvement in the stratosphere.
A more recent study (Klais et al. (1980)) reports similar deactivation information
for $O_2(^1\Delta, v > 0)$ and recommends a reaction channel for $O_2(^1\Delta, v > 0) + O_3$ of
less than 10% of the deactivation rate. Thus it appears that the primary fate
of both of these vibrationally excited oxygen species is physical quenching.

NO_x and $O(^1D)$ Reactions

The kinetic data base for NO_x reactions, which was relatively good at the
time of the previous evaluation (NASA RP 1049), has nevertheless shown a modest
improvement since that time. The major change in the recommendations is for the
reaction $OH + HNO_3$; the negative temperature dependent expression results in a
significantly greater rate at low temperatures when compared to the previously
recommended temperature independent value. Confirmation is needed. In addition,
the effect of this new rate expression on modelling calculations is strongly
dependent on the reaction path assumed. Direct mechanistic information is still
needed. A new study of the rate constant for the reaction $O_3 + NO$ reports
results within 12 percent of the recommended values over the range 200 - 300 K.
This satisfies the need for independent confirmation mentioned in NASA RP 1049.

There is still a poor data base for reactions of HO_2NO_2. Only a single temperature dependent study for the oxygen atom reaction has been reported; studies with other reactive atmospheric species (particularly OH) are still needed to assess the role of HO_2NO_2 in atmospheric chemistry.

There are minor (less than 10 percent) changes in some of the $O(^1D)$ recommended rate constant values. These changes and the reduced uncertainty factors reflect the expanded data base, which includes results reported from up to four laboratories. It should be noted that the evidence previously reported for significant quenching components in the interactions with H_2O, N_2O and CH_4 has been retracted.

HO_x Reactions

This class of reactions continues to be a major source of uncertainty in stratospheric chemistry. Perhaps the principal reason is that the HO_2 radical is relatively difficult to produce and to monitor over a wide range of conditions, but at the same time shows a dependence in several of its key reactions on reaction conditions. We have already discussed the seemingly contradictory results for the $OH + HO_2$ reaction under different reaction conditions (mainly pressure). Whether these discrepancies are real or are merely experimental artifacts remains to be seen. The $HO_2 + HO_2$ reaction exhibits dependences on pressure, temperature, and water vapor. Water vapor dependence is not particularly important in the stratosphere, because of the low water concentrations. However, the temperature dependence (and its possible dependence in turn on pressure) can make a large difference under stratospheric conditions. In previous evaluations we have recommended a single value (2.5×10^{-12} cm^3 s^{-1}) for this rate constant, with large uncertainties in the T-dependence. The present

evaluation for the first time takes account of the combined P- and T-dependences, by means of an altitude-dependent rate constant (see note for this reaction for exact recommendations). This empirical approach is regarded as an interim measure.

Unusual T-dependences shown by the HO_2 + ClO, OH + HNO_3, and OH + CO reaction have already been mentioned.

ClO_x Reactions

The kinetics data base for ClO_x reactions has improved significantly in the last few years, although there are still several areas of concern. The issue of isomer formation in the ClO + NO_2 + M reaction has already been mentioned, and furthermore the photolysis products of $ClONO_2$ have still not been resolved. If there are two isomers of $ClNO_3$ formed in the ClO + NO_2 + M reaction, and if the second isomer is a linear molecule which is relatively easily photolyzed, then the ClO_x - NO_x coupling is significantly reduced in the lower stratosphere. However, the ClO_x system will still be strongly coupled to the HO_x system through the ClO + HO_2 reaction, which produces HOCl. With the recent results which show a strong negative temperature dependence for the formation of HOCl at stratospheric temperatures, HOCl may play an important role in stratospheric photochemistry. The general consensus of opinion is that HOCl rapidly photolyzes. Consequently HOCl should not be viewed as a temporary reservoir for odd chlorine which tends to reduce the catalytic efficiency of ClO_x for destroying odd oxygen, but rather as a species which participates in a catalytic cycle which destroys odd oxygen. Therefore, while certain HOCl and $ClNO_3$ formation and destruction processes cannot be considered to be well defined, the overall effect of the uncertainties on the modelling calculations should not be too great. Additional studies of the product distribution in the ClO + NO_2 + M, and HO_2 + ClO reactions, and the HOCl and

ClONO$_2$ photolysis processes are required.

Other areas of uncertainty involving ClO$_x$ species include the possibility of complex formation between ClO and O$_2$. However, at present there is no firm experimental evidence to support the ClO·O$_2$ complex hypothesis, and experimental data are needed to provide further insight into this possibility.

There is some evidence (Ravishankara and Wine, 1980) for different reactivity of the $^2P_{1/2}$ and $^2P_{3/2}$ states of atomic chlorine, especially in the important reaction Cl + CH$_4$ → HCl + CH$_3$. This possible dependence on quantum state may explain previous discrepancies between low pressure flow discharge studies of the Cl + CH$_4$ reaction (where equilibrium between the states is more effectively maintained) and competitive chlorination studies (where one state may be preferentially depleted). This hypothesis, while attractive in some respects, requires further verification.

Methane Oxidation

The oxidation of methane in the stratosphere involves the formation and reaction of CH$_3$O and CH$_3$O$_2$ radicals as well as the subsequent reactions of products such as H$_2$CO and CH$_3$OOH. In general, the data base for the CH$_3$O$_2$ reactions continues to improve, although it is still relatively poor. Since the evaluation in NASA RP-1049, new data has become available for CH$_3$O$_2$ + NO and CH$_3$O$_2$ + NO$_2$ + M. New reactions evaluated include CH$_3$O$_2$ + SO$_2$ and CH$_3$O$_2$ + CH$_3$O$_2$. Information on the temperature dependence of the rate constants for CH$_3$O$_2$ and CH$_3$O reactions is generally limited or non-existent. The situation is much better for the reactions of H$_2$CO, where the temperature dependence of the rate constants are reasonably well characterized.

A characteristic of many of the reactions involved in methane oxidation is the possibility of multiple reaction channels. Accordingly, there is a need

for mechanistic information to complement the growing data base for rate co-efficients. There is also no assurance that the relative importance of the reaction channels for a particular reaction will be invariant with temperature or pressure. All these features emphasize the need for continuing mechanistic, temperature and pressure studies.

Sulfur Chemistry

The reactions evaluated are those representing the oxidation of a few simple sulfur compounds which have been observed in the atmosphere and which are considered important in the global sulfur cycle.

The only change since the NASA RP-1049 evaluation is a substantial lowering of the rate constant at 298K for the reactions of OH with OCS and CS_2. Work is in progress on the temperature dependences of both the rate constant and the reaction channels for these two reactions. New studies are also being made of the reaction OH + H_2S. A subsequent evaluation will very likely reflect the results of these current investigations.

Since the possibility of multiple reaction channels exists for many of the reactions of simple sulfur compounds, there is a general need for quantitative mechanistic measurements as a function of temperature to complement the rate constant determinations.

Three-Body Reactions

Perhaps the major problem in this reaction category is the previously mentioned question of isomer formation in the ClO + NO_2 + M reaction. As before (previous evaluations), we are recommending two rates, one assuming that the reaction produces only $ClONO_2$, and the other (slower) rate assuming that the major product is an isomer of $ClNO_3$ which rapidly photolyzes.

This unresolved question remains as one of the major uncertainties in stratospheric chemistry.

Beginning with Evaluation No. 2 (JPL 79-27), we have presented 3-body rate constant data in terms of the Troe formulation. (Details are reviewed in a later section on format). This approach has the advantage that a single equation, involving four input parameters, is adequate to represent the temperature dependence and pressure fall-off behavior of all 3-body reactions. This avoids the otherwise necessary use of empirical equations derived by curve-fitting procedures. Further, it facilitates a comparison of experimental data with theory.

Photochemical Processes

The identity of the primary products in the photodissociation of several species remains to be established. For example, for HO_2NO_2, $BrONO_2$ and N_2O_5 no product studies have been carried out, and for $ClONO_2$ there are conflicting results.

The temperature dependence of the absorption cross sections of HO_2NO_2, CH_2O and CF_2O should be determined. Also, the UV spectra of species such as $FONO_2$ and HOBr are not known. The absorption cross sections of O_3 and their temperature dependence deserve further study in view of their important for atmospheric modeling and for interpreting Dobson and BUV data.

RATE CONSTANT DATA

Format

The rate constant tabulation for second-order reactions (Table 1) gives the following information:

1. Reaction stoichiometry and products (if known).

2. Arrhenius A-factor.

3. Temperature dependence and associated uncertainty ("activation temperature" $E/R \pm \Delta E/R$).

4. Rate constant at 298K.

5. Uncertainty factor at 298K.

6. Note giving basis of recommendation and any other pertinent information.

Third-order reactions (Table 2) are given in the form

$$k_o(T) = k_o^{300}(T/300)^{-n} \; cm^6 \; s^{-1},$$

(where the value is suitable for air as the third body), together with the recommended value of n. Where pressure fall-off corrections are necessary, an additional entry gives the limiting high pressure rate constant in a similar form:

$$k_\infty(T) = k_\infty^{300}(T/300)^{-m} \; cm^3 \; s^{-1}.$$

To obtain the effective second-order rate constant for a given condition of temperature and pressure (altitude), the following formula is used:

$$k(z) = k(M,T) = \left(\frac{k_o(T)[M]}{1 + k_o(T)[M]/k_\infty(T)}\right) 0.6^{\{1 + [log_{10}(k_o(T)[M]/k_\infty(T))]^2\}^{-1}}.$$

The number 0.6 which appears in this formula has been changed from the value 0.8 which appears in JPL 79-27. This small change better accommodates the data and is more consistent with theory.

Thus, a compilation of rate constants of this type requires the stipulation of the four parameters, $k_o(300)$, n, $k_\infty(300)$, and m. These can be found in Table 2. The discussion that follows outlines the general methods we have

used in establishing this table, and the notes to the table discuss specific data sources.

Low-Pressure Limiting Rate Constant $[k_x^o(T)]$

Troe (1977) has described a simple method for obtaining low-pressure limiting rate constants. In essence this method depends on the definition:

$$k_x^o(T) \equiv \beta_x \; k_x^{o,sc}(T)$$

where sc signifies "strong" collisions, x denotes the bath gas, and β_x is an efficiency parameter $(o<\beta<1)$, which provides a measure of energy transfer.

The coefficient β_x is related to the average energy transferred in a collision with gas x, $<\Delta E>_x$, via:

$$\frac{\beta_x}{1 - \beta_x^{1/2}} = \frac{<\Delta E>_x}{F_E \; kT} \;.$$

Notice that $<\Delta E>$ is quite sensitive to β. F_E is the correction factor of the energy dependence of the density of states (a quantity of the order of 1.1 for most species of stratospheric interest).

For many of the reactions of possible stratospheric interest reviewed here, there exist data in the low-pressure limit (or very close thereto), and we have chosen to _evaluate_ _and_ _unify_ this data by calculating $k_x^{o,sc}(T)$ for the appropriate bath gas x and computing the value of β_x corresponding to the experimental value [Troe (1977)].

From the β_x values (most of which are for N_2, i.e., β_{N_2}), we compute $<\Delta E>_x$ according to equation (5). Values of $<\Delta E>_{N_2}$ of approximately 0.3-1 kcal mole^{-1} are generally expected. If multiple data exist, we average the values of

$\langle \Delta E \rangle_{N_2}$ and recommend a rate constant corresponding to the β_{N_2} computed via equation (5).

Where no data exist, we have estimated the low-pressure rate constant by taking $\beta_{N_2} = 0.3$ at T = 300 K; a value based on those cases where data exist.

Temperature Dependence of Low-Pressure Limiting Rate Constants: n

The value of n recommended here comes from a calculation of $\langle \Delta E \rangle_{N_2}$ from the data at 300 K, and a computation of β_{N_2} (200 K) assuming that $\langle \Delta E \rangle_{N_2}$ is independent of temperature. This β_{N_2} (200 K) value is combined with the computed value of k_o^{sc}(200 K) to give the expected value of the actual rate constant at 200 K. This latter in combination with the value of 300 K yields the value of n.

This procedure can directly be compared with measured values of k_o(200 K) when those exist. Unfortunately, very few values of 200 K are available. There are often temperature-dependent studies, but some ambiguity exists when one attempts to extrapolate these down to 200 K. If data is to be extrapolated out of the measured temperature range, a choice must be made as to the functional form of the temperature dependence. There are two general ways of expressing the temperature dependence of rate constants. Either the Arrhenius expression $k_o(T) = A_{exp}(-E/RT)$ or the form $k_o(T) = A' \cdot T^{-n}$ is employed. Since neither of these extrapolation techniques is soundly based, and since they often yield values that differ substantially, we have used the method explained heretofore as the basis of our recommendations.

In JPL 79-27, we have computed the extrapolated values at 200 K using both T^{-n} and Arrhenius forms when data are available over any reasonable temperature range. When these values are compared with the recommendation, it can be seen that the data are well accommodated by our methods.

High-Pressure Limiting Rate Constants $[k_\infty(T)]$

High-pressure rate constants can often be obtained experimentally, but those for the relatively small species of atmospheric importance usually reach the high-pressure limit at inaccessibly high pressures. This leaves two sources of these numbers, the first being guesses based upon some model, and the second extrapolation of fall-off data up to higher pressures. Stratospheric conditions generally render reactions of interest much closer to the low-pressure limit, and thus are fairly insensitive to the high-pressure value. This means that while the extrapolation is long, and the value of $k_\infty(T)$ not very precise, a "reasonable guess" of $k_\infty(T)$ will then suffice. In some cases we have declined to guess since the low-pressure limit is always in effect over the entire range of stratospheric conditions.

Temperature Dependence of High-Pressure Limiting Rate Constants: m

There is very little data upon which to base a recommendation for values of m. Values in Table 1 are estimated, based on models for the transition state of bond association reactions and whatever data are available.

Error Estimates

For second-order rate constants in Table 1, an estimate of the uncertainty at any given temperature may be obtained from the following expression:

$$f_T = f_{298} \exp\left(\frac{\Delta E}{R}\left|\frac{1}{T} - \frac{1}{298}\right|\right).$$

An upper or lower bound (corresponding approximately to one standard deviation) of the rate constant at any temperature T can be obtained by multiplying or dividing the value of the rate constant at that temperature by the factor f_T. The quantities f_{298} and $\Delta E/R$ are, respectively, the uncertainty in

the rate constant at 298K and in the Arrhenius temperature coefficient, as listed in Table 1. Figure 1 illustrates the application of this equation for the OH + O_3 reaction, as an example. The dashed line represents the NASA recommendation and the shaded area corresponds to the uncertainty limits.

For three-body reactions (Table 2) a somewhat analogous procedure is used. Uncertainties expressed as increments to k_o and k_∞ are given for these rate constants at room temperature. The additional uncertainty arising from the temperature extrapolation is expressed as an uncertainty in the temperature coefficients $\underline{n}$ and $\underline{m}$.

Units

The rate constants are given in units of concentration expressed as molecules per cubic centimeter and time in seconds. Thus, for first-, second-, and third-order reactions the units of k are s^{-1}, cm^3 molecule^{-1} s^{-1}, and cm^6 molecule^{-2} s^{-1}, respectively.

Figure 1.

Illustration of Rate Constant Uncertainty as a Function of Temperature. Shaded Area Represents Range of Possible Values (1σ) for the OH + O_3 Reaction.

$$OH + O_3 \rightarrow HO_2 + O_2$$

ZAHNISER & HOWARD $6.4 \times 10^{-14} \left(\frac{T}{300}\right)^4$

RAVISHANKARA ET AL. $1.8 \times 10^{-12} \exp\left(-\frac{930}{T}\right)$

DeMORE $4.5 \times 10^{-12} \exp\left(-\frac{1230}{T}\right)$

KURYLO

MARGITAN & ANDERSON

NASA $1.6 \times 10^{-12} \exp\left(-\frac{940}{T}\right)$

ANDERSON & KAUFMAN $1.3 \times 10^{-12} \exp\left(-\frac{956}{T}\right)$

1000/T
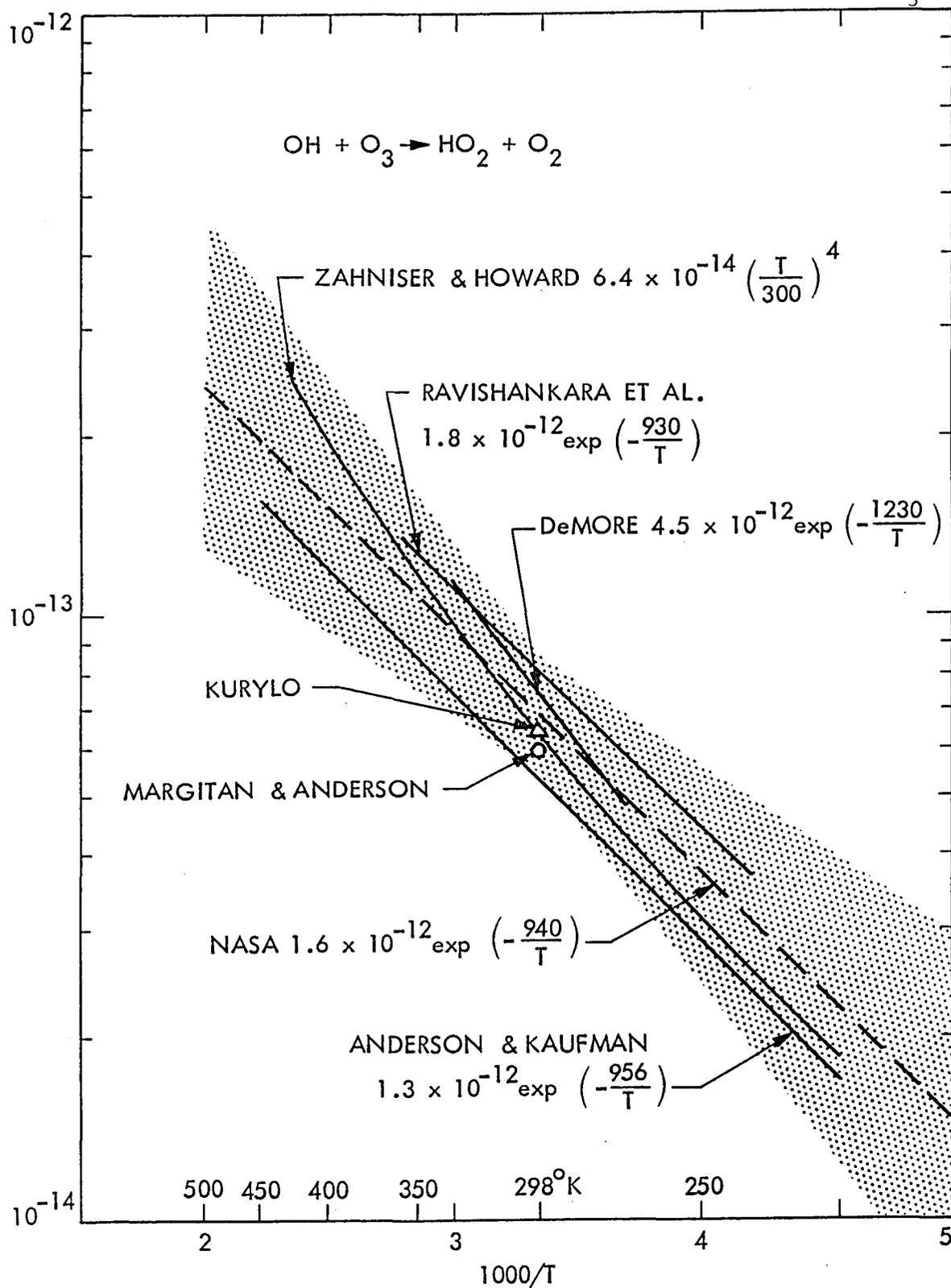
Table 1. Rate Constants for Second-Order Reactions.

Reaction	A-Factor	$E/R \pm \Delta(E/R)$	$k(298K)$	Uncertainty Factor (298K)	Notes
$O + O_2 \xrightarrow{M} O_3$	(See Table 2)				---
$O + O_3 \rightarrow O_2 + O_2$	1.5×10^{-11}	2218 ± 150	8.8×10^{-15}	1.15	1
$O_3 + NO \rightarrow NO_2 + O_2$	2.3×10^{-12}	1450 ± 200	1.8×10^{-14}	1.2	2
$OH + NO_2 \xrightarrow{M} HNO_3$	(See Table 2)				---
$O + NO_2 \rightarrow NO + O_2$	9.3×10^{-12}	0^{+0}_{-150}	9.3×10^{-12}	1.1	3
$O + HNO_3 \rightarrow OH + NO_3$	-	-	$<3.0 \times 10^{-17}$	-	4
$O + HO_2NO_2 \rightarrow products$	7.4×10^{-12}	2630 ± 300	1.1×10^{-15}	2.0	5
$N + O_2 \rightarrow NO + O$	4.4×10^{-12}	3220 ± 340	8.9×10^{-17}	1.25	6
$N + NO \rightarrow N_2 + O$	3.4×10^{-11}	0 ± 100	3.4×10^{-11}	1.3	7
*$OH + HNO_3 \rightarrow products$	1.5×10^{-14}	$-(650 \pm 300)$	1.3×10^{-13}	1.4	8
*$OH + HO_2NO_2 \rightarrow products$	-	-	8.0×10^{-13}	10.0	9
$N + NO_2 \rightarrow N_2O + O$	2.1×10^{-11}	800 ± 350	1.4×10^{-12}	1.25	10
$N + O_3 \rightarrow NO + O_2$	-		$<1.0 \times 10^{-15}$	-	11
$NO_2 + O_3 \rightarrow NO_3 + O_2$	1.2×10^{-13}	2450 ± 140	3.2×10^{-17}	1.15	12
$HO_2 + NO_2 \xrightarrow{M} HO_2NO_2$	(See Table 2)				---
$NO + NO_3 \rightarrow 2NO_2$	-	-	2.0×10^{-11}	3.0	13
*$O(^1D) + N_2O \rightarrow N_2 + O_2$	5.1×10^{-11}	0 ± 50	5.1×10^{-11}	1.4	14
*$O(^1D) + N_2O \rightarrow NO + NO$	6.6×10^{-11}	0 ± 50	6.6×10^{-11}	1.4	14
*$O(^1D) + H_2O \rightarrow OH + OH$	2.2×10^{-10}	0 ± 50	2.2×10^{-10}	1.2	14
*$O(^1D) + CH_4 \rightarrow OH + CH_3$	1.4×10^{-10}	0 ± 50	1.4×10^{-10}	1.2	14
$O(^1D) + CH_4 \rightarrow H_2 + CH_2O$	1.4×10^{-11}	0 ± 50	1.4×10^{-11}	1.2	14

*Indicates a change from the previous Panel evaluation (NASA RP 1049)

†Indicates a new entry that was not in the previous evaluation.

Table 1. (Continued).

Reaction	A-Factor	E/R ± Δ(E/R)	k(298K)	Uncertainty Factor (298K)	Notes
$O(^1D) + H_2 \rightarrow OH + H$	9.9×10^{-11}	0 ± 50	9.9×10^{-11}	1.3	14
*$O(^1D) + N_2 \rightarrow O + N_2$	1.8×10^{-11}	$-(107 \pm 50)$	2.6×10^{-11}	1.2	14
$O(^1D) + N_2 \xrightarrow{M} N_2O$	(See Table 2)				
*$O(^1D) + O_2 \rightarrow O + O_2$	3.2×10^{-11}	$-(67 \pm 50)$	4.0×10^{-11}	1.2	14
$O(^1D) + O_3 \rightarrow O_2 + O_2$	1.2×10^{-10}	0 ± 50	1.2×10^{-10}	1.2	14
$O(^1D) + O_3 \rightarrow O_2 + O + O$	1.2×10^{-10}	0 ± 50	1.2×10^{-10}	1.2	14
$O(^1D) + HCl \rightarrow OH + Cl$	1.4×10^{-10}	0 ± 50	1.4×10^{-10}	1.3	14
$O(^1D) + CFCl_3 \rightarrow products$	2.2×10^{-10}	0 ± 50	2.2×10^{-10}	1.3	14
$O(^1D) + CF_2Cl_2 \rightarrow products$	1.4×10^{-10}	0 ± 50	1.4×10^{-10}	1.3	14
$O(^1D) + CCl_2O \rightarrow products$	3.6×10^{-10}	0 ± 50	3.6×10^{-10}	1.4	14
$O(^1D) + CFClO \rightarrow products$	1.9×10^{-10}	0 ± 50	1.9×10^{-10}	1.4	14
$O(^1D) + CF_2O \rightarrow products$	2.3×10^{-10}	0 ± 50	2.3×10^{-10}	1.4	14
$O(^1D) + NH_3 \rightarrow OH + NH_2$	2.5×10^{-10}	0 ± 50	2.5×10^{-10}	1.3	14
*$O(^1D) + CO_2 \rightarrow O + CO_2$	7.4×10^{-11}	$-(117 \pm 50)$	1.1×10^{-10}	1.2	14
$O + NO_3 \rightarrow O_2 + NO_2$	1.0×10^{-11}	0 ± 150	1.0×10^{-11}	1.6	15
$O + N_2O_5 \rightarrow products$	-	-	$<3.0 \times 10^{-16}$	-	16
$O_3 + HNO_2 \rightarrow O_2 + HNO_3$	-	-	$<5.0 \times 10^{-19}$	-	17
$OH + HO_2 \rightarrow H_2O + O_2$	4.0×10^{-11}	0 ± 250	4.0×10^{-11}	2.5	18
*$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	(See note)	(See note)	2.5×10^{-12}	2.0	19
*$NO + HO_2 \rightarrow NO_2 + OH$	3.5×10^{-12}	$-(250 \pm 100)$	8.1×10^{-12}	1.2	20
$HO_2 + O_3 \rightarrow OH + 2O_2$	1.1×10^{-14}	580^{+500}_{-100}	1.6×10^{-15}	1.4	21
$OH + O_3 \rightarrow HO_2 + O_2$	1.6×10^{-12}	940 ± 300	6.8×10^{-14}	1.25	22
*$O + OH \rightarrow O_2 + H$	2.3×10^{-11}	$-(110 \pm 200)$	3.3×10^{-11}	1.2	23
*$O + HO_2 \rightarrow OH + O_2$	4.0×10^{-11}	0 ± 350	4.0×10^{-11}	2.0	24
$O + H_2O_2 \rightarrow OH + HO_2$	2.8×10^{-12}	2125 ± 400	2.2×10^{-15}	2.0	25

*Indicates a change from the previous Panel evaluation (NASA RP 1049).

†Indicates a new entry that was not in the previous evaluation.

Table 1. (Continued).

Reaction	A-Factor	$E/R \pm \Delta(E/R)$	$k(298K)$	Uncertainty Factor (298K)	Notes
$H + O_2 \overset{M}{\rightarrow} HO_2$	(See Table 2)				
$H + O_3 \rightarrow OH + O_2$	1.4×10^{-10}	470 ± 200	2.9×10^{-11}	1.25	26
$*OH + OH \rightarrow H_2O + O$	4.5×10^{-12}	275 ± 275	1.8×10^{-12}	1.4	27
$OH + OH \overset{M}{\rightarrow} H_2O_2$	(See Table 2)				
$*OH + H_2O_2 \rightarrow H_2O + HO_2$	2.7×10^{-12}	145 ± 100	1.7×10^{-12}	1.25	28
$OH + CO \rightarrow CO_2 + H$	$1.35 \times 10^{-13}(1 + P_{atm})$	0 ± 200	$1.35 \times 10^{-13}(1 + P_{atm})$	1.25	29
$OH + CH_4 \rightarrow CH_3 + H_2O$	2.4×10^{-12}	1710 ± 200	7.7×10^{-15}	1.2	30
$OH + H_2 \rightarrow H_2O + H$	1.2×10^{-11}	2200 ± 200	7.5×10^{-15}	1.2	31
$Cl + O_3 \rightarrow ClO + O_2$	2.8×10^{-11}	257 ± 100	1.2×10^{-11}	1.15	32
$O + ClO \rightarrow Cl + O_2$	7.7×10^{-11}	130 ± 130	5.0×10^{-11}	1.2	33
$*NO + ClO \rightarrow NO_2 + Cl$	6.5×10^{-12}	$-(280 \pm 100)$	1.7×10^{-11}	1.15	34
$OH + HCl \rightarrow H_2O + Cl$	2.8×10^{-12}	425 ± 100	6.6×10^{-13}	1.15	35
$*OH + HOCl \rightarrow H_2O + ClO$	3.0×10^{-12}	150^{+350}_{-150}	1.8×10^{-12}	10.0	36
$*Cl + CH_4 \rightarrow HCl + CH_3$	9.6×10^{-12}	1350 ± 150	1.0×10^{-13}	1.1	37
$\dagger Cl + C_2H_6 \rightarrow HCl + C_2H_5$	7.7×10^{-11}	90 ± 90	5.7×10^{-11}	1.1	38
$*Cl + HO_2 \rightarrow HCl + O_2$	4.8×10^{-11}	0 ± 250	4.8×10^{-11}	2.0	39
$ClO + NO_2 \overset{M}{\rightarrow} ClONO_2$	(See Table 2)				
$O + ClONO_2 \rightarrow products$	3.0×10^{-12}	808 ± 200	2.0×10^{-13}	1.5	40
$OH + ClONO_2 \rightarrow products$	1.2×10^{-12}	333 ± 200	3.9×10^{-13}	1.5	41
$Cl + ClONO_2 \rightarrow products$	1.7×10^{-12}	607 ± 388	2.2×10^{-13}	2.0	42
$O + HCl \rightarrow OH + Cl$	1.14×10^{-11}	3370 ± 350	1.4×10^{-16}	2.0	43
$O + HOCl \rightarrow OH + ClO$	1.0×10^{-11}	2200 ± 800	6.0×10^{-15}	10.0	44
$Cl + H_2 \rightarrow HCl + H$	3.5×10^{-11}	2290 ± 200	1.6×10^{-14}	1.5	45
$Cl + H_2O_2 \rightarrow HCl + HO_2$	1.1×10^{-11}	980 ± 500	4.1×10^{-13}	1.5	46
$Cl + HNO_3 \rightarrow products$	$<1.0 \times 10^{-11}$	2170^{+2500}_{-500}	$<7.0 \times 10^{-15}$	–	47

*Indicates a change from the previous Panel evaluation (NASA RP 1049).

$\dagger$Indicates a new entry that was not in the previous evaluation.

Table 1. (Continued).

Reaction	A-Factor	E/R ± Δ(E/R)	k(298K)	Uncertainty Factor (298K)	Notes
$Cl + H_2CO \rightarrow HCl + HCO$	9.2×10^{-11}	68 ± 100	7.3×10^{-11}	1.15	48
$Cl + CH_3Cl \rightarrow CH_2Cl + HCl$	3.4×10^{-11}	1260 ± 200	4.9×10^{-13}	1.2	49
$Cl + NO \overset{M}{\rightarrow} NOCl$	(See Table 2)				
$Cl + ClNO \rightarrow NO + Cl_2$	3.0×10^{-11}	0^{+500}_{-250}	3.0×10^{-11}	2.0	50
$Cl + O_2 \overset{M}{\rightarrow} ClOO$	(See Table 2)				
$ClOO \overset{M}{\rightarrow} Cl + O_2$	2.7×10^{-9}	2650 ± 800	3.7×10^{-13}	7.0	51
*$Cl + ClOO \rightarrow Cl_2 + O_2$	1.4×10^{-10}	0 ± 250	1.4×10^{-10}	3.0	52
*$Cl + ClOO \rightarrow ClO + ClO$	8.0×10^{-12}	0 ± 250	8.0×10^{-12}	3.0	52
†$Cl + Cl_2O \rightarrow Cl_2 + ClO$	9.8×10^{-11}	0 ± 250	9.8×10^{-11}	1.2	53
†$O + Cl_2O \rightarrow ClO + ClO$	-	-	4.0×10^{-12}	1.5	54
*$ClO + HO_2 \rightarrow HOCl + O_2$	4.6×10^{-13}	$-(710 \pm 250)$	5.0×10^{-12}	1.4	55
†$ClO + H_2CO \rightarrow products$	$\leq 1.0 \times 10^{-12}$	≥ 2060	$\leq 1.0 \times 10^{-15}$	-	56
$ClO + OH \rightarrow products$	-	-	9.1×10^{-12}	3	57
$ClO + CH_4 \rightarrow products$	$\leq 1.0 \times 10^{-12}$	≥ 3700	$\leq 4.0 \times 10^{-18}$	-	58
$ClO + H_2 \rightarrow products$	$\leq 1.0 \times 10^{-12}$	≥ 4800	$\leq 1.0 \times 10^{-19}$	-	58
$ClO + CO \rightarrow products$	$\leq 1.0 \times 10^{-12}$	≥ 3700	$\leq 4.0 \times 10^{-18}$	-	58
$ClO + N_2O \rightarrow products$	$\leq 1.0 \times 10^{-12}$	≥ 4260	$\leq 6.0 \times 10^{-19}$	-	58
$ClO + BrO \rightarrow Br + OClO$	6.7×10^{-12}	0 ± 250	6.7×10^{-12}	1.5	59
$ClO + BrO \rightarrow Br + Cl + O_2$	6.7×10^{-12}	0 ± 250	6.7×10^{-12}	1.5	59
$ClO + ClO \rightarrow products$	-	-	-	-	60
$ClO + O_3 \rightarrow ClOO + O_2$	1.0×10^{-12}	≥ 4000	$< 1.0 \times 10^{-18}$	-	61
$ClO + O_3 \rightarrow OClO + O_2$	1.0×10^{-12}	≥ 4000	$< 1.0 \times 10^{-18}$	-	61
$Cl + OClO \rightarrow ClO + ClO$	5.9×10^{-11}	0 ± 250	5.9×10^{-11}	1.25	62
$NO + OClO \rightarrow NO_2 + ClO$	2.5×10^{-12}	600 ± 300	3.4×10^{-13}	1.5	·63
$O + OClO \rightarrow ClO + O_2$	2.5×10^{-11}	1166 ± 300	5.0×10^{-13}	1.5	64

*Indicates a change from the previous Panel evaluation (NASA RP 1049).

†Indicates a new entry that was not in the previous evaluation.

Table 1. (Continued).

Reaction	A-Factor	E/R ± Δ(E/R)	k(298K)	Uncertainty Factor (298K)	Notes
*OH + CH_3Cl → CH_2Cl + H_2O	1.8×10^{-12}	1112 ± 200	4.3×10^{-14}	1.2	65
*OH + CH_2Cl_2 → $CHCl_2$ + H_2O	4.5×10^{-12}	1032 ± 200	1.4×10^{-13}	1.2	65
·OH + $CHCl_3$ → CCl_3 + H_2O	3.3×10^{-12}	1034 ± 200	1.0×10^{-13}	1.2	65
*OH + $CHFCl_2$ → $CFCl_2$ + H_2O	8.9×10^{-13}	1013 ± 200	3.0×10^{-14}	1.3	65
*OH + CHF_2Cl → CF_2Cl + H_2O	7.8×10^{-13}	1530 ± 200	4.6×10^{-15}	1.2	65
*OH + CH_2ClF → $CHClF$ + H_2O	2.0×10^{-12}	1134 ± 150	4.4×10^{-14}	1.2	65
OH + CH_3CCl_3 → CH_2CCl_3 + H_2O	5.4×10^{-12}	1820 ± 200	1.2×10^{-14}	1.3	66
OH + C_2Cl_4 → products	9.4×10^{-12}	1200 ± 200	1.7×10^{-13}	1.25	67
OH + C_2HCl_3 → products	5.0×10^{-13}	$-(445 \pm 200)$	2.2×10^{-12}	1.25	68
OH + $CFCl_3$ → products	1.0×10^{-12}	>3650	$<5.0 \times 10^{-18}$	-	69
OH + CF_2Cl_2 → products	1.0×10^{-12}	>3560	$<6.5 \times 10^{-18}$	-	69
Br + O_3 → BrO + O_2	1.4×10^{-11}	755 ± 200	1.1×10^{-12}	1.2	70
O + BrO → Br + O_2	3.0×10^{-11}	0 ± 250	3.0×10^{-11}	3.0	71
BrO + NO → NO_2 + Br	8.7×10^{-12}	$-(265 \pm 130)$	2.1×10^{-11}	1.15	72
BrO + NO_2 $\overset{M}{\to}$ $BrONO_2$	(See Table 2)				
BrO + BrO → 2 Br + O_2	1.0×10^{-12}	$-(244 \pm 150)$	2.3×10^{-12}	1.25	73
BrO + BrO → Br_2 + O_2	1.8×10^{-13}	$-(244 \pm 150)$	4.0×10^{-13}	1.25	73
BrO + O_3 → Br + 2 O_2	1.0×10^{-12}	>1600	$<5.0 \times 10^{-15}$	-	74
Br + H_2O_2 → HBr + HO_2	1.0×10^{-11}	>2650	$<1.5 \times 10^{-15}$	-	75
*Br + HO_2 → HBr + O_2	-	-	-	-	76
†Br + H_2CO → HBr + HCO	1.4×10^{-11}	750 ± 250	1.1×10^{-12}	1.5	77
OH + HBr → H_2O + Br	8.5×10^{-12}	0 ± 250	8.5×10^{-12}	2.0	78
O + HBr → OH + Br	7.6×10^{-12}	1570 ± 300	3.9×10^{-14}	1.5	79
BrO + HO_2 → HOBr + O_2	-	-	5.0×10^{-12}	5.0	80
BrO + OH → products	-	-	9.0×10^{-12}	5.0	81

*Indicates a change from the previous Panel evaluation (NASA RP 1049).

†Indicates a new entry that was not in the previous evaluation.

Table 1. (Continued).

Reaction	A-Factor	E/R ± Δ(E/R)	k(298K)	Uncertainty Factor (298K)	Notes
*OH + $CH_3Br \rightarrow CH_2Br + H_2O$	6.1×10^{-13}	825 ± 200	3.8×10^{-14}	1.25	82
$F + O_3 \rightarrow FO + O_2$	2.8×10^{-11}	226 ± 200	1.3×10^{-11}	2.0	83
$F + O_2 \overset{M}{\rightarrow} FO_2$	(See Table 2)				
$F + H_2 \rightarrow HF + H$	2.0×10^{-10}	620 ± 250	2.5×10^{-11}	1.5	84
$F + CH_4 \rightarrow HF + CH_3$	3.0×10^{-10}	400 ± 300	8.0×10^{-11}	2.0	85
$F + H_2O \rightarrow HF + OH$	2.2×10^{-11}	200 ± 200	1.1×10^{-11}	5.0	86
$O + FO \rightarrow F + O_2$	5.0×10^{-11}	0 ± 250	5.0×10^{-11}	3.0	87
*NO + $FO \rightarrow NO_2 + F$	2.6×10^{-11}	0 ± 250	2.6×10^{-11}	1.5	88
$FO + FO \rightarrow 2 F + O_2$	1.5×10^{-11}	0 ± 250	1.5×10^{-11}	3.0	89
$FO + O_3 \rightarrow F + 2 O_2$	-	-	-	-	90
$FO + O_3 \rightarrow FO_2 + O_2$	-	-	-	-	90
$O + FO_2 \rightarrow FO + O_2$	5.0×10^{-11}	0 ± 250	5.0×10^{-11}	5.0	91
$O(^1D) + HF \rightarrow OH + F$	1.0×10^{-10}	0 ± 100	1.0×10^{-10}	3.0	92
$CH_3 + O_2 \overset{M}{\rightarrow} CH_3O_2$	(See Table 2)				
†$CH_3 + O_2 \rightarrow$ products	-	-	$<10^{-16}$	-	93
$CH_3 + O \rightarrow H_2CO + H$	1.0×10^{-10}	0 ± 250	1.0×10^{-10}	1.4	94
*$CH_3O_2 + NO \rightarrow CH_3O + NO_2$	7.4×10^{-12}	0 ± 500	7.4×10^{-12}	1.25	95
$CH_3O_2 + NO_2 \overset{M}{\rightarrow} CH_3O_2NO_2$	(See Table 2)				
*$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$	7.7×10^{-14}	$-(1300^{+500}_{-1300})$	6.0×10^{-12}	3.0	96
†$CH_3O_2 + SO_2 \rightarrow$ products	-	-	$<5.0 \times 10^{-17}$	-	97
†$CH_3O_2 + CH_3O_2 \rightarrow$ products	-	-	4.0×10^{-13}	1.25	98
*$CH_3O + O_2 \rightarrow H_2CO + HO_2$	9.2×10^{-13}	2200 ± 750	5.7×10^{-16}	2.0	99
$OH + H_2CO \rightarrow HCO + H_2O$	1.0×10^{-11}	0 ± 200	1.0×10^{-11}	1.25	100
$O + H_2CO \rightarrow$ products	3.0×10^{-11}	1550 ± 250	1.6×10^{-13}	1.25	101
$HCO + O_2 \rightarrow CO + HO_2$	5.0×10^{-12}	0 ± 250	5.0×10^{-12}	1.4	102

*Indicates a change from the previous Panel evaluation (NASA RP 1049).

†Indicates a new entry that was not in the previous evaluation.

Table 1. (Continued).

Reaction	A-Factor	E/R ± Δ(E/R)	k(298K)	Uncertainty Factor (298K)	Notes
*OH + CH_3OOH → products	2.1×10^{-12}	145 ± 100	1.3×10^{-12}	5.0	103
O + H_2S → OH + SH	2.6×10^{-11}	2170 ± 750	1.8×10^{-14}	2.0	104
O + OCS → CO + SO	2.1×10^{-11}	2200 ± 150	1.3×10^{-14}	1.12	105
O + CS_2 → CS + SO	3.1×10^{-11}	640 ± 150	3.6×10^{-12}	1.12	106
OH + H_2S → SH + H_2O	1.1×10^{-11}	220 ± 220	5.3×10^{-12}	1.25	107
*OH + OCS → products	-	-	$<1.0 \times 10^{-14}$	-	108
*OH + CS_2 → products	-	-	$<1.5 \times 10^{-15}$	-	109

*Indicates a change from the previous Panel evaluation (NASA RP 1049).

†Indicates a new entry that was not in the previous evaluation.

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NOTES TO TABLE 1

1. This recommendation is slightly different from the NBS TN 866 and NASA RP-1010 recommendation ($k = 1.9 \times 10^{-11} \exp(-2300/T)$ and is based on the measurements of McCrumb and Kaufman (1972) and Davis et al. (1973).

2. Recommended Arrhenius expression is that of Birks et al. (1976). Room temperature value is an average of Birks et al. (1976), Bemand et al. (1974), Becker et al. (1974) and Stedman and Niki (1973). The slightly lower pre-exponential factor recommended in NASA RP-1010 was based on an alternative analysis of the primary data in Birks et al. and inclusion of older room temperature data. The present recommendation accepts the data analysis given in Birks' paper. Results reported recently by Lippman et al. (1980) are in good agreement (within 12 percent) with the recommended values over the temperature range 200 to 300 K.

3. Based on results of Davis et al. (1973), Bemand et al. (1974) and Slanger et al. (1973), there may be a slight negative temperature coefficient, but the evidence at low temperature is uncertain.

4. Accepts the upper limit reported by Chapman and Wayne (1974).

5. Recommended value is based on the study of Trevor, Chang and Barker (1980). The large uncertainty factor is due to this being a single study. Additional confirmation is needed.

6. Activation energy based on Becker et al. (1969). Value and uncertainty at 298 K assigned from average of Clyne and Thrush (1961), Wilson (1967), Becker et al. (1969), Clark and Wayne (1970) and Westenberg et al. (1970). Independent confirmation of the temperature dependence is needed.

7. Recommendation is based on the results of Lee et al. (1978c). A recent study by Husain and Slater (1980) reports a k_{298} 30 percent higher than the recommended value.

8. Changed from NASA RP-1049. New recommendation is based on the results of Wine et $al.$ (1980a). A large discrepancy exists between this study and the results of Smith and Zellner (1975) and Margitan et $al.$ (1975), particularly at low temperature. The uncertainties in E/R and k(298) have been chosen to reflect this. Additional confirmation of the rate constant and temperature dependence is needed. The products of the reaction are not known; the Arrhenius expression of Wine et $al.$ suggests a complex mechanism.

9. Estimated by analogy with the reaction $OH + H_2O_2$. This value is consistent with the upper limit of 3×10^{-12} reported by Graham, Winer, and Pitts (1978a).

10. Accepts the 298 K results of Clyne and McDermid (1975) for both the value of the rate constant and the identity of the products. A pre-exponential factor of 2×10^{-11} was chosen as a reasonable estimate and the temperature dependence was derived from a fit to the room temperature rate constant. Clearly, temperature dependent studies are needed. A recent study (Husain and Slater, 1980) reports a room temperature rate constant value of 3.8×10^{-11} cm^3 $molecule^{-1} s^{-1}$ for the overall reaction of N with NO_2. This high value may indicate the presence of catalytic cycles as discussed in Clyne and McDermid (1975). This reaction is not an important one, and until this discrepancy is resolved we have chosen not to change the recommendation.

11. Recommendation based on results of Stief et $al.$ (1978). Note that this is an upper limit based on instrumental sensitivity. NASA RP-1010 recommended an estimated temperature dependent expression based on the room temperature value of Phillips and Schiff (1962) which was about a factor of 500 greater than the upper limit recommended here. Results of Garvin and Broida (1963) cast doubt on the fast rate reported by Phillips

and Schiff and as such support Stief's results. Independent confirmation is needed.

12. Based on least squares fit to data in studies of Davis et al. (1974b), Graham and Johnston (1974) and Huie and Herron (1974).

13. Value reported by Graham and Johnston (1978).

14. These recommendations are based on averages of the results reported by Streit et al. (1976), Davidson et al. (1977a) and Davidson et al. (1978) for N_2O, H_2O, CH_4, H_2, N_2, O_2, O_3, HCl, $CFCl_3$, CF_2Cl_2, NH_3 and CO_2; by Amimoto et al. (1979) for N_2O, H_2O, CH_4, N_2, O_2, O_3 and CO_2; by Wine and Ravishankara (1980) for N_2O, H_2O, N_2, O_3 and CO_2; by Brock and Watson (1980) for N_2, O_2 and CO_2; and by Lee and Slanger (1978 and 1979) for H_2O and O_2. The weight of the evidence from these studies seems to reject the results of Heidner and Husain (1973), Heidner et al. (1973) and Fletcher and Husain (1976a, 1976b).

The branching ratio for the reaction of $O(^1D)$ with N_2O to give $N_2 + O_2$ or NO + NO is an average of the values reported by Davidson et al. (1979); Pirkle et al. (1977); and Marx et al. (1979). This latest result by Marx et al. is significantly different from the earlier results. Further study is needed

The branching ratio for reaction of $O(^1D)$ with CH_4 to give OH + CH_3 or $CH_2O + H_2$ is from Lin and DeMore (1973). The branching ratio for reaction of $O(^1D)$ with O_3 to give $O_2 + O_2$ or $O_2 + O + O$ is from Davenport et al. (1974). For the reactions of $O(^1D)$ with CCl_2O, CFClO and CF_2O, rate constants are reported only by the Cambridge Laboratory by Fletcher and Husain (1978). Thus, for consistency, the recommended values for these rate constants were derived using a scaling procedure. This procedure preserves the relative placement of these rate constants among the set of Cambridge Laboratory data but employs an average ratio (0.50) of the above recommendations to Cambridge Laboratory rate constants. These reactions have been studied

only at 298 K. Based on consideration of similar $O(^1D)$ reactions, it is assumed that E/R equals zero, and therefore the value shown for the A-factor has been set equal to k(298 K).

The chlorocarbon rate constants are for total disappearance of $O(^1D)$ and probably include physical quenching. Values have been reported for the fraction of the total rate of disappearance of $O(^1D)$ proceeding through the reactive channel forming ClO for $CFCl_3$ (.60 ± .15) and CF_2Cl_2 (.55 ± .15) by Donovan (1980). It is not possible to give corresponding values for the reaction $O(^1D)$ with CCl_2O and CFClO. It should be noted that the evidence previously reported (Amimoto et al. (1979) for significant quenching components in the interactions of $O(^1D)$ with N_2O, H_2O and CH_4 has been retracted (Amimoto et al. (1980).

15. Based on study of Graham and Johnston (1978) and 298 K and 329 K. While limited in temperature range, the data indicate no temperature dependence. Furthermore, by analogy with the reaction of O with NO_2 it is assumed that this rate constant is in fact independent of temperature. Clearly, temperature dependent studies are needed.

16. Based on Kaiser and Japar (1978).

17. Based on Kaiser and Japar (1977) and Streit et al. (1979).

18. This recommendation is unchanged from the earlier ones; however, it would be prudent for modelers to consider also a higher value, $\sim 1 \times 10^{-10}$, in view of the accumulating evidence for such a value in several high pressure studies. The present recommendation is based solely on the low pressure study by Chang and Kaufman (1978), which should have provided a firm upper limit. The work of Burrows et al. (1977, 1979) requires re-evaluation in view of the change in value for their reference reaction $(OH + H_2O_2)$. The change in $k(OH + H_2O_2)$ also invalidates the Hack et al. (1978) study (See Sridharan et al., 1980). At higher pressure, values of

$1\text{-}2 \times 10^{-10}$ have been measured in several studies (Hochanadel et al., 1974, 1980; DeMore and Tschuikow-Roux, 1974; DeMore, 1979) and are being confirmed in a new DeMore (1980) study at pressures as low as 75 torr. There is no obvious explanation for a pressure dependence since it would require a third-order rate constant in excess of 2×10^{-29}. A recent high pressure study by Lii et al. (1980a) also reports 1×10^{-10}, although the significance of that is unclear in view of the extremely limited nature of the data. Obviously a definitive study over the whole pressure range is required. Direct kinetic measurements are essential.

19. This reaction has unusual pressure, temperature and water vapor dependences (Hamilton and Lii, 1977; Cox and Burrows, 1979; Thrush and Wilkinson, 1979; Lii et al., 1979). At atmospheric pressure, E/R ∿1200. Very limited data at 10 torr indicate E/R ∿600. The reaction appears to be pressure dependent below ∿25 torr at room temperature (possibly purely third-order) with the pressure dependence extending to higher pressures at lower temperatures. For modeling purposes, we have grossly over-extrapolated the available data to provide rate constant expressions applicable to the temperatures and pressures of the $40°N$ stratosphere (the water vapor dependence is not included). They are (z = altitude in km):

$$0 < z < 10 \qquad k = 2.3 \times 10^{-12}\exp(0.15\,z)$$

$$10 < z < 15 \qquad k = 1 \times 10^{-11}$$

$$15 < z < 50 \qquad k = 1 \times 10^{-11}\exp[-0.088(z - 15)]$$

These are purely empirical parameters, and results obtained with them (e.g., H_2O_2 densities) should be viewed with utmost caution. Uncertainties are at least a factor of two.

20. The recommendation is based on the work of Howard's group (Howard and
    Evenson, 1977; Howard, 1979, 1980), since it is the most extensive.
    The results are confirmed by several other studies (Margitan and
    Anderson, 1978; Kaufman and Reimann, 1978; Leu, 1979; Glaschick-Schimpf
    et al., 1979), although the latter two are $\sim$20 - 30% higher. The Burrows
    et al. (1977, 1979) measurement of the ratio of $k(HO_2 + NO)$ to $k(OH + H_2O_2)$
    under presumed steady state conditions does not agree with direct measure-
    ments of those reactions, indicating an incorrect characterization of their
    kinetics. A high pressure study is needed in view of the many unusual
    effects seen in other HO_2 reactions.

21. The recommendation is based on an average room temperature value of five
    studies which span a range of a factor of two (Zahniser and Howard, 1980;
    Margitan and Anderson, 1978; DeMore and Tschuikow-Roux, 1974; Simonaitis
    and Heicklen, 1973; DeMore, 1979). The temperature dependence is that of
    Zahniser and Howard, which is the most direct work and is confirmed by
    the last three studies, which were relative to $k(HO_2 + HO_2)$, when the
    high pressure T dependence is used for that reaction. The A-factor is
    unusually low for reasons which remain unclear.

22. The room temperature value is an average of five studies (Anderson and
    Kaufman, 1973; Kurylo, 1973; DeMore, 1975; Margitan and Anderson, 1978;
    and Ravishankara et al., 1979b). The Anderson and Kaufman and Ravishankara
    et al. studies are in excellent agreement on the temperature dependence
    (E/R = 955 and 930, respectively) and are confirmed by DeMore's data over
    a more limited range. Preliminary results (Zahniser and Howard, 1980) are
    in excellent agreement with the recommendation below room temperature.
    Their measured rate constants also agree very well with the recommended
    values at higher temperatures, although their data indicate a curved Arrhenius
    plot over the entire temperature range.

23. The room temperature value is an average (Howard and Smith, 1980; Lewis and Watson, 1980), and the T dependence is from the latter study. These recent results are in good agreement with earlier studies (Kaufman, 1964; Clyne, 1963; Westenberg et al., 1970).

24. The recommendation is based on the work of Hack et al. (1979) in which $k(O + HO_2)$ was measured in ten experiments by two "direct" techniques (involving some data correction) with both methods yielding $k = (4.2 \pm 1.0) \times 10^{-11}$. Five other experiments measured $k(O + HO_2)/k(O + OH) = (0.85 \pm 0.4)$, yielding $k(O + HO_2) = (2.8 \pm 1.3) \times 10^{-11}$ using this evaluation's $k(O + OH)$. Two other investigations of $k(O + HO_2)$ are not considered reliable. With the new OH + H_2O_2, the Burrows et al. (1977, 1979) work is internally inconsistent. The Lii et al. (1980) study, as reported, is based on only four experiments involving a curve fitting procedure that is insensitive to the desired rate constant: deviations of measured points from the calculated curves greatly exceed the differences in those curves due to factors of 2 variation in $k(O + HO_2)$ and are not explainable.

25. This expression is that of Davis et al. (1974a). In view of the difficulties in studying H_2O_2 reactions, another study is needed to confirm the rate constant, especially at low temperatures. The A-factor seems low, especially in light of the OH + H_2O_2 parameters.

26. The recommendation is an average of the recent results of Lee et al. (1978b) and Keyser (1979a), which are in excellent agreement over the 200-400 K range. An earlier study by Clyne and Monkhouse (1977) is in very good agreement on the T dependence in the range 300-650 K but lies about 60% below the recommended values. Although we have no reason not to believe the Clyne and Monkhouse values, we prefer the two studies that are in excellent agreement, especially since they were carried out over the

T range of interest. Recent results by Finlayson-Pitts and Kleindienst (1979) agree well with the present recommendations. Their reports of a channel forming HO_2 + O ($\sim$ 25%) have been withdrawn (Howard and Finlayson-Pitts, 1980).

27. This value is based on an average of the measurements of Westenberg and de Haas (1973a), McKenzie et al. (1973), Clyne and Down (1974), Trainor and von Rosenberg (1974), and Zellner and Wagner (1980), with the T dependence taken from that last study.

28. The new results by Keyser (1980) and Sridharan et al. (1980) clearly demonstrate that previous determinations are in error. Those papers contain a detailed discussion of the reasons for the discrepancies and an assessment of the impact of this new value on other relative rate constant measurements.

29. The recommended expression is $k = 1.35 \times 10^{-13} \times [1 + P(\text{atm})]$, which allows for the factor of 2 increase in k seen in several studies at 1 atm pressures of non-inert gases. The most detailed study (Biermann et al. (1978) found that the pressure effect requires either (a) small amounts of O_2 ($\sim$ 0.25 torr) or (b) the presence of other impurities. Further study of the combined pressure and temperature effects is needed.

30. This reaction is one of the few not requiring further work. All T dependence studies are in excellent agreement (Greiner, 1970; Davis et al., 1974c; Margitan et al., 1974; Zellner and Steinert, 1976). Due to this agreement and the curved nature of the Arrhenius plot, the value of Davis et al. is recommended since that measurement extends to the lowest temperature.

31. The recommendation is based on three T dependence studies which are in very good agreement (Smith and Zellner, 1974; Greiner, 1969; and

Atkinson et al., 1975). The k(298) is based on these studies plus other room temperature determinations. Because of the wider temperature range of the Smith and Zellner study, this evaluation weights their results heavily.

32. Unchanged from NASA 1049. The results reported for k(298 K) by Watson et al. (1976), Zahniser et al. (1976), Kurylo and Braun (1976a) and Clyne and Nip (1976a) are in good agreement, and have been used to determine the preferred value at this temperature. The values reported by Leu and DeMore (1976) (due to the wide error limits) and Clyne and Watson (1974a) (the value is inexplicably high) are not considered. The four Arrhenius expressions are in fair agreement within the temperature range 205 - 300 K. In this temperature range, the rate constants at any particular temperature agree to within (30 - 40%). Although the values of the activation energy obtained by Watson et al., and Kurylo and Braun are in excellent agreement, the value of k in the study of Kurylo and Braun is consistently ($\sim$ 17%) lower than that of Watson et al. This may suggest a systematic underestimate of the rate constant, as the value of the other three studies agree so well at 298 K. A more disturbing difference is the scatter in the values reported for the activation energy (338-831 cal mole^{-1}). However, there is no reason to prefer any one set of data to any other; therefore, the preferred Arrhenius expression shown above was obtained by computing the mean of the four results between 205 and 298 K. Inclusion of higher temperature ($\leq$ 466 K) experimental data would yield the following Arrhenius expression: k = (3.34 ± 1.0) x 10^{-11} exp(-310 ± 76)/T).

33. Unchanged from NASA 1049. The preferred values were derived in the same manner as the previous NASA evaluation. This expression is based on values of 5.0 x 10^{-11} cm^{3}molecule^{-1}s^{-1} and 4.4 x 10^{-11}cm^{3}molecule^{-1}s^{-1} at

298 and 230 K, respectively. These values were deduced from the experimental data of Bemand et al. (1973), Clyne and Nip (1976b), and Zahniser and Kaufman (1977). The E/R values reported by Clyne and Nip and Zahniser and Kaufman are in poor agreement. Before this reaction can be considered to be well understood, additional data are required.

34. Changed from NASA 1049. The absolute rate coefficients determined in the four discharge flow mass spectrometric studies (Clyne and Watson (1974a), Leu and DeMore (1978b), Watson and Ray (1980) and Clyne and MacRobert (1980)) and the discharge flow laser magnetic resonance study (Howard and Lee (1980)) are in excellent agreement at 298 K, and are averaged to yield the preferred value of 1.67×10^{-11}. The value reported by Zahniser and Kaufman (1977) from a competitive study is not used in the derivation of the preferred value as it is $\sim$ 33% higher. The magnitudes of the temperature dependences reported by Leu and DeMore (1978b) and Howard and Lee (1980) are in excellent agreement, with an average E/R value of -283 K. Although the E/R value reported by Zahniser and Kaufman (1977) is in fair agreement with the other values, it was not considered as it is dependent upon the E/R value assumed for the $Cl + O_3$ reaction. The Arrhenius expression was derived by combining the preferred E/R value (-283 K) with the preferred 298 K value (1.67 x 10^{-11}), i.e. $6.46 \times 10^{-12} \exp(283/T)$.

35. Unchanged from NASA 1049. There is good agreement between all five groups of workers at $\sim$ 298 K (Takacs and Glass (1973c), Zahniser et al. (1974), Smith and Zellner (1974), Ravishankara et al. (1977a), and Hack et al. (1976)) and the preferred value at this temperature is the average of the five. The Arrhenius expression was derived by giving an equal weighting to data reported by Zahniser et al., Ravishankara et al., and Smith and Zellner.

36. Changed from NASA 1049. There are no experimental data for this reac-

    tion. This is an estimated value based on the OH + H_2O_2 reaction, which

    should have similar E/R and A values, i.e. k = 3 x 10^{-12} exp (-150/T).

37. Minor modifications from NASA 1049. The values reported from the thir-

    teen absolute rate coefficient studies for k at 298 K range from 0.99 to

    1.48 x 10^{-13} with a mean value of 1.15 x 10^{-13}. However, based upon the

    stated confidence limits reported in each study, the range of values

    far exceeds that to be expected. A preferred average value of 1.04 x

    10^{-13} can be determined from the absolute rate coefficient studies for

    k at 298 K by giving equal weighting to the values reported in Leu et al.

    (1978a), Watson et al. (1976), Manning and Kurylo (1977), Whytock et al.

    (1977), Zahniser et al. (1978), Michael and Lee (1977), Keyser (1978),

    and Ravishankara and Wine (1980). The values derived for k at 298 K

    from the competitive chlorination studies of Pritchard et al. (1954),

    Knox (1955), Pritchard et al. (1955), Knox and Nelson (1959), and Lin

    et al. (1978a) range from 0.95 - 1.13 x 10^{-13}, with an average value of

    1.02 x 10^{-13}. The preferred value of 1.04 x 10^{-13} was obtained by taking

    a mean value from the most reliable absolute and relative rate coefficient

    studies.

    There have been nine absolute studies of the temperature dependence of k.

    In general the agreement between most of these studies can be considered

    to be quite good. However, for a meaningful analysis of the reported

    studies it is best to discuss them in terms of two distinct temperature

    regions, (a) below 300 K, and (b) above 300 K. Three resonance fluor-

    escence studies have been performed over the temperature range ∿ 200 -

    500 K (Whytock et al. (1977), Zahniser et al. (1978) and Keyser (1978))

    and in each case a strong nonlinear Arrhenius behavior was observed.

Ravishankara and Wine (1980) also noted nonlinear Arrhenius behavior over a more limited temperature range. This behavior tends to explain partially the large variance in the values of E/R reported between those other investigators who predominantly studied this reaction below 300 K (Watson et al. (1976) and Manning and Kurylo (1977)) and those who only studied it above 300 K (Clyne and Walker (1973), Poulet et al. (1974), and Lin et al. (1978a)). The agreement between all studies below 300 K is good, with values of (a) E/R ranging from 1229 - 1320 K, and (b) k(230 K) ranging from $(2.64 - 3.32) \times 10^{-14}$. The mean of the two discharge flow values (Zahniser et al. (1978) and Keyser (1978)) is 2.67×10^{-14}, while the mean of the four flash photolysis values (Watson et al. (1976), Manning and Kurylo (1977), Whytock et al. (1977), and Ravishankara and Wine (1980)) is 3.22×10^{-14} at 230 K. There have not been any absolute studies at stratospheric temperatures other than those which utilized the resonance fluorescence technique. Ravishankara and Wine (1980) have suggested that the results obtained using the discharge flow and competitive chlorination techniques may be in error at the lower temperatures (< 240 K) due to a non-equilibration of the $^2P_{1/2}$ and $^2P_{3/2}$ states of atomic chlorine. Ravishankara and Wine observed that at temperatures below 240 K the apparent bimolecular rate constant was dependent upon the chemical composition of the reaction mixture, i.e. if the mixture did not contain an efficient spin equilibrator, e.g. Ar or CCl_4, the bimolecular rate constant decreased at high CH_4 concentrations (high values of k^1). The chemical composition in each of the flash photolysis studies contained an efficient spin equilibrator, whereas this was not the case in the discharge flow studies. However, the reactor walls in the discharge flow studies could have been expected to have acted as an effi-

cient spin equilibrator. Consequently, until the hypothesis of Ravi-

shankara and Wine is proven it is assumed that the discharge flow and

competitive chlorination results are reliable. Above 300 K the three

resonance fluorescence studies reported (a) "averaged" values of E/R

ranging from 1530 - 1623 K, and (b) values for k (500 K) ranging from

$(7.74 - 8.76) \times 10^{-13}$. These mass spectrometric studies have been per-

formed above 300 K with E/R values ranging from 1409 - 1790 K. The data

of Poulet et al. (1974) are sparse and scattered, that of Clyne and Walker

(1973) show too strong a temperature dependence (compared to all other

absolute and competitive studies) and k(298 K) is ∿ 20% higher than the

preferred value at 298 K, while that of Lin et al. (1978a) is in fair

agreement with the resonance fluorescence results. In conclusion, it

should be stated that the best values of k from the absolute studies,

both above and below 300 K, are obtained from the resonance fluorescence

studies. The competitive chlorination results differ from those ob-

tained from the absolute studies in that linear Arrhenius behavior is

observed. This difference is the major discrepancy between the two

types of experiments. The values of E/R range from 1503 to 1530 K, and

k (230 K) from 2.11 - 2.54) $\times 10^{-14}$ with a mean value of 2.27×10^{-14}.

It can be seen from the above discussion that the average values at 230 K

are: 3.19×10^{-14} (flash photolysis), 2.67×10^{-14} (discharge flow) and

2.27×10^{-14} (competitive chlorination). These differences increase at

lower temperatures. Until the hypothesis of Ravishankara and Wine (1980)

is re-examined, the preferred Arrhenius expression attempts to best fit

the results obtained between 200 and 300 K from all sources. The aver-

age value of k at 298 K is 1.04×10^{-13}, and at 230 K is 2.71×10^{-14}

(this is a simple mean of the three average values). The preferred

Arrhenius expression is $9.6 \times 10^{-12} \exp(-1350/T)$--this expression essentially yields values similar to those obtained in the discharge flow-resonance fluorescence studies. If only flash photolysis-resonance fluorescence results are used then an alternate expression of 6.4×10^{-12} $(\exp(-1220/T)$ can be obtained $(k(298 \text{ K}) = 1.07 \times 10^{-13}$, and $k(230 \text{ K}) = 3.19 \times 10^{-14})$.

38. New entry. The absolute rate coefficients reported in all five studies (Davis et al. (1970), Manning and Kurylo (1977), Watson et al. (1978), Lewis et al. (1980), and Ray et al. (1980) in good agreement at 298 K. The value reported by Davis et al. was probably overestimated by $\sim 10\%$ (the authors assumed that I_f was proportional to $[Cl]^{0.9}$, whereas a linear relationship between I_f and $[Cl]$ probably held under their experimental conditions). The preferred value at 298 K was taken to be a simple mean of the five values (the value reported by Davis et al. was reduced by 10%), i.e., 5.7×10^{-11}. The two values reported for E/R are in good agreement; E/R = 61 K (Manning and Kurylo) and E/R = 130 K (Lewis et al.). A simple least squares fit to all the data would unfairly weight the data of Lewis et al. due to the larger temperature range covered. Therefore, the preferred value of $7.7 \times 10^{-11} \exp(-90/T)$ is an expression which best fits the data of Lewis et al. and Manning and Kurylo between 220 and 350 K.

39. Changed from NASA 1049. The values of $k(Cl + HO_2)/k(Cl + H_2O_2)$ reported by Leu and DeMore (1976), Poulet et al. (1978b), and Burrows et al. (1979) are in poor agreement with values ranging from 48-170. The discrepancy between the two mass-spectrometric results may be attributed to inaccurate estimates of the mass-spectrometric sensitivity for HO_2. If the NASA preferred value of 4.1×10^{-13} for $k(Cl + H_2O_2)$ at 298 K is combined with the experimentally determined ratios, then values of 2.0,

7.0 and 4.3 x 10^{-11} are obtained for $k(Cl + HO_2)$. Cox (1980) deter-

mined $k(Cl + HO_2)$ relative to $k(Cl + H_2)$ over the temperature range

274-338 K, and reported a value of 3.0 exp(+2120/T) for $k(Cl + HO_2)$/

$k(Cl + H_2)$. Combining this value with the NASA preferred value of

3.5 x 10^{-11} exp(-2290/T) for $k(Cl + H_2)$ yields a value of 1.05 x 10^{-10}

exp(-170/T) for $k(Cl + HO_2)$. However, considering the uncertainties

in both $k(Cl + HO_2)/(Cl + H_2)$ and $k(Cl + H_2)$ the value of $k(Cl + HO_2)$

is effectively independent of temperature with a value of (6.0 ± 3.0)

x 10^{-11}. Cox (1980) reevaluated the earlier work of Cox and Derwent

(1977) to determine a value for $k(Cl + HO_2)$ of ≥ 4.0 x 10^{-11} (due to a

revised value for $k(Cl + H_2)$). The preferred value of 4.8 x 10^{-11} for

$k(Cl + HO_2)$ at 298 K was obtained by averaging the reevaluated values

of Leu and DeMore, Poulet et al., Burrows et al., and Cox. The lack

of a temperature dependence, as observed by Cox, is consistent with that

expected for an atom-radical reaction. Based upon the data reported by

Burrows et al. an upper limit of 4.8 x 10^{-13} has been placed on the rate

constant for production of ClO + OH (1% of the total rate constant).

40. Unchanged from NASA 1049. The results reported by Molina et al. (1977b)

and Kurylo (1977) are in good agreement, and this data has been used to

derive the preferred Arrhenius expression. The value reported by Ravi-

shankara et al. (1977b) at 245 K is a factor of 2 greater than those

from the other studies, and this may possibly be attributed to (a)

secondary kinetic complications, (b) presence of NO_2 as a reactive

impurity in the $ClONO_2$, or (c) formation of reactive photolytic products.

None of the studies reported identification of the reaction products.

41. Unchanged from NASA 1049. The results reported by Zahniser et al. (1977)

and Ravishankara et al. (1977b) are in good agreement at $\sim$ 245 K (within

25%) considering the difficulties associated with handling $ClONO_2$. The preferred value is that of Zahniser et al. Neither study reported any data on the reaction products.

42. Unchanged from NASA 1049. Considering the experimental difficulties associated with handling $ClONO_2$, and the low precision of the data of Ravishankara et al. (1976), the results are in fair agreement at 245 K. Therefore, the preferred value is taken to be that reported by Kurylo and Manning (1977). Neither study reported any information which could be used to identify products.

43. Unchanged from NASA 1049. Fair agreement exists between the results of Brown and Smith (1975), Wong and Belles (1971), Ravishankara et al. (1977a) and Hack et al. (1977) at 300 K (some of the values quoted for k (300 K) were obtained by extrapolation of the experimentally determined Arrhenius expressions), but these are a factor of $\sim$ 7 lower than that of Balakhnin et al. (1971). Unfortunately the values reported for E/R are in complete disagreement, ranging from 2260 - 3755 K. The preferred value was based on the results reported by Brown and Smith, Wong and Belles, Ravishankara et al., and Hack et al. but not those reported by Balakhnin et al.

44. Unchanged from NASA 1049. There are no experimental data; this is an estimated value based on rates of O-atom reactions with similar compounds.

45. Unchanged from NASA 1049. This value is based on the results obtained below 300 K by Watson et al. (1975) and Lee et al. (1977). Although the results of these two studies are in agreement below 300 K, the data at higher temperatures are in somewhat poorer agreement. Lee et al. argue that their results are correct due to their agreement with Westenberg and de Haas (1968), and with the H + HCl study of

Ambidge et al. (1976). However, the values of k at 298 K reported in these studies are not in particularly good agreement, the data of Westenberg and de Haas are not beyond question, and all of the H + HCl studies appear to be subject to surface problems in the flow reactor, thus restricting the precision and accuracy of the results. In contrast, the results of Watson et al. agree well (after extrapolation) with the results of Benson et al. (1969) and Steiner and Rideal (1939) at higher temperatures. Further, the preferred value of $k(Cl + H_2)$ derived from using the data of Watson et al. and Lee et al., when combined with relative rate data for the reaction of Cl with H_2 and CH_4, gives rates for $Cl + CH_4$ at 300 K and above which are significantly lower than those measured directly. Thus, although this reaction is not particularly important in the stratosphere, additional studies are needed before the Arrhenius parameters can be considered to be well defined.

46. Unchanged from NASA 1049. The absolute rate coefficients determined at ∿ 298 K by Watson et al. (1976), Leu and DeMore (1976), Michael et al. (1977), Poulet et al. (1978a) and Keyser (1979) range in value from $(3.6 - 6.2) \times 10^{-13}$. The studies of Michael et al., Keyser, and Poulet et al. are presently considered to be the most reliable. The preferred value for the Arrhenius expression is taken to be that reported by Keyser. The A-factor reported by Michael et al. is considerably lower than that expected from theoretical considerations and may possibly be attributed to decomposition of H_2O_2 at temperatures above 300 K. The data of Michael et al. at and below 300 K are in good agreement with the Arrhenius expression reported by Keyser. More data are required before the Arrhenius parameters can be considered to be well established.

47. Unchanged from NASA 1049. Neither study (Leu and DeMore (1976), and Poulet et al. (1978a)) can be considered to be definitive. Poulet et al.

postulated that Leu and DeMore were observing removal of HNO_3 via a heterogeneous process. While this hypothesis is certainly tenable, the value of E/R reported by Poulet et al. is much higher than would be expected (resulting in a surprisingly low value for k at 298 K). Although this reaction is not important in atmospheric chemistry, additional studies are required to provide accurate Arrhenius parameters. Until further data becomes available, the preferred value is based on assuming that the data of Leu and DeMore represents an upper limit.

48. Unchanged from NASA 1049. The results from three of the four published studies (Michael et al. (1979), Anderson and Kurylo (1979), and Niki et al. (1978a)) are in good agreement at $\sim$ 298 K, but $\sim$ 50% greater than the value reported by Foon et al. (1979). The preferred value at 298 K was obtained by combining the absolute values reported by Michael et al., and Anderson and Kurylo, with the value obtained by combining the ratio of $k(Cl + H_2CO)/k(Cl + C_2H_6)$ reported by Niki et al. (1.3 ± 0.1) with the NASA preferred value of 5.7×10^{-11} for $k(Cl + C_2H_6)$ at 298 K. A preferred value of 7.3×10^{-11} was determined for k at 298 K. This value is in good agreement with the provisional value reported by Fasano and Nogar (1980) using the novel technique of infrared laser photolysis – infrared chemiluminescence. The E/R values of Michael et al. (E/R = 0), and Anderson and Kurylo (E/R = 131 K) are averaged to yield the preferred E/R value of 68 K. The A-factor was adjusted to yield the preferred value at 298 K.

49. Unchanged from NASA 1049. The results reported by all three groups (Clyne and Walker (1973), Watson et al. (1978) and Manning and Kurylo

(1977) are in good agreement at 298 K. However, the value of the

activation energy measured by Watson et al. and Manning and Kurylo

is significantly lower than that measured by Clyne and Walker. Both

groups of workers measured the rate constant for the Cl + CH_4 and

similarly, the activation energy measured by Watson et al. and Manning

and Kurylo was significantly lower than that measured by Clyne and

Walker. It is suggested that the discharge flow-mass spectrometric

technique is subject to a systematic error, and it is recommended that

the flash photolysis results be used for stratospheric calculations in

the 200 - 300 K temperature range (see discussion of the Cl + CH_4 studies).

In the discussion of the Cl + CH_4 reaction it was suggested that some of

the apparent discrepancy between the results of Clyne and Walker and

the flash photolysis studies can be explained by nonlinear Arrhenius

behavior. However, it is less likely that this can be invoked for this

reaction as the pre-exponential A-factor (as measured in the flash photoly-

sis studies) is already $\sim 3.5 \times 10^{-11}$ and the significant curvature which

would be required in the Arrhenius plot to make the data compatible

would result in an unreasonably high value for A ($> 2 \times 10^{-10}$).

50. Unchanged from NASA 1049. Value based on the discharge flow - resonance

fluorescence study of Clyne and Cruse (1972). The competitive study of

Burns and Dainton (1952) was deemed less reliable, and the results from

the recent study of Grimley and Houston (1980) are lower than those of

Clyne and Cruse by a factor of 5. Unfortunately, until the differences

between the reported results are resolved there is a large uncertainty

in the preferred value. No reliable data on the temperature dependence.

51. Unchanged from NASA 1049. Cox et al. (1979) reported a value of 3.7×10^{-28}

x T x exp(3217/T) for K = k(Cl + O_2 + M)/k(ClOO + M). This corresponds to

a value of $94.8 \begin{smallmatrix} + & 1.6 \\ - & 1.0 \end{smallmatrix}$ kJ mol^{-1} for ΔH_f^o (ClOO) which is in excellent agreement with the value of 94.0 ± 2.0 kJ mol^{-1} reported by Ashford et al. (1978).

52. Changed from NASA 1049. Values of 1.56×10^{-10}, 9.8×10^{-11}, and 1.67×10^{-10} have been reported for k_a(Cl + ClOO $\rightarrow$ Cl$_2$ + O$_2$) by Johnston et al. (1969), Cox et al. (1979), and Ashford et al. (1978), respectively. Values of 108, 20.9, 17, and 15 have been reported for k_a(Cl + ClOO $\rightarrow$ Cl$_2$ + O$_2$)/k (Cl + ClOO $\rightarrow$ 2 ClO) by Johnston et al., Cox et al., Ashford et al., and Nicholas and Norrish (1968). Obviously the value of 108 by Johnston et al. is in error, with a preferred value of 17.6 being obtained by averaging the other three values (this is in agreement with a value that can be derived from a study by Porter and Wright (1953)). The absolute values of k_a and k_b are dependent upon the choice of ΔH_f^o (ClOO) (the values of ΔH_f^o (ClOO) reported by Cox et al. and Ashford et al. are in excellent agreement, i.e. 94.8 and and 94.0 kJ mol^{-1}, respectively). The preferred value of k_a (Cl + ClOO $\rightarrow$ Cl$_2$ + O$_2$) is taken to be the average of the three reported values, i. e. 1.4×10^{-10} cm^3 molecule^{-1}s^{-1}. Consequently, the pre-ferred value of k_b (Cl + ClOO $\rightarrow$ 2 ClO) is k_a/17.6, i.e. 8.0×10^{-12} cm^{3}molecule^{-1}s^{-1}. The E/R values are estimated to be zero, which is consistent with other experimentally determined E/R values for atom-radical reactions

53. New entry. The preferred value of 9.8×10^{-11} cm^{3}molecule^{-1}s^{-1} was determined from two independent absolute rate coefficient studies re-ported by Ray et al. (1980), using the discharge flow-resonance fluor-escence and discharge flow-mass spectrometric techniques.

The earlier value reported by Basco and Dogra (1971) has been rejected. The Arrhenius parameters have not been experimentally determined; however, the value of k at 298 K is consistent with the value expected for the A-factor of such a reaction, i.e. close to the gas kinetic collision frequency for such an atom-molecule reaction.

54. New entry. The absolute rate coefficients reported by Miziolek and Molina (1978), and Delf and Schindler (1980) are in excellent agreement at 298 K. The preferred value at 298 K is the average of these two values, i.e. 4.0×10^{-12} cm^3 molecule^{-1} s^{-1}. The values reported by Basco and Dogra (1971a) and Freeman and Phillips (1968) have not been included in the derivation of the preferred value due to data analysis difficulties in each of these studies.

55. Changed from NASA 1049. There have been four low pressure discharge flow studies, each using a different experimental detection technique, and one high pressure molecular modulation study (Burrows et al. (1980)) at 298 K. The values reported at 298 K, in units of 10^{-12} cm^3 molecule^{-1}s^{-1}, are 0.85 ± 0.19 (Poulet et al. (1978)), 3.8 ± 0.5 (Reimann and Kaufman (1978)), 4.5 ± 0.9 (Leck et al. (1980)), 6.3 ± 1.3 (Stimpfle et al. (1979)), and $5.4 \, {}^{+ \, 4}_{- \, 2}$ (Burrows et al. (1980)). Clearly the value of Poulet et al. should be rejected, and the preferred value taken to be the mean of the other four values, i.e. $k = 5.0 \times 10^{-12} cm^3$ molecule^{-1}s^{-1}. The agreement between the low pressure values and the one atmosphere value suggests the absence of a third order complex forming process. The only temperature dependence study (Stimpfle et al.) observed a non-linear Arrhenius behavior. Their data was best described by a four parameter equation of the form, $k = Ae^{-B/T} + CT^n$, possibly suggesting that two different mechanisms may be occurring.

The expression forwarded by Stimpfle et al. was $3.3 \times 10^{-11} \exp(-850/T)$ + $4.5 \times 10^{-12} (T/300)^{-3.7}$. Two possible preferred values can be forwarded for the temperature dependence of k, (a) An expression of the form suggested by Stimpfle et al. but where the values of A and C are adjusted to yield a value of 5.0×10^{-11} at 298 K, i.e. 2.5×10^{-11} $\exp(-850/T)$ + $3.5 \times 10^{-12} (T/300)^{-3.7}$, or a simple Arrhenius expression which fits the data obtained at and below 300 K (normalized to 5.0×10^{-11} at 298 K), i.e. $4.6 \times 10^{-13} \exp(710/T)$. The latter expression is preferred and entered in the summary table. The two most probable pairs of reaction products are, (1) $HOCl + O_2$ and (2) $HCl + O_3$. Both Leu (1980) and Leck et al. used mass spectrometric detection of ozone to place upper limits of 1.5% (298 K), 3.0% (248 K) and 2.0% (298 K), respectively on k_2/k.

56. New entry. Poulet et al. (1980) have determined an upper limit of $10^{-15} cm^3 molecule^{-1} s^{-1}$ for k at 298 K using the discharge flow-EPR technique.

57. Unchanged from NASA 1049. The value is based on the low pressure discharge flow-resonance fluorescence/mass spectrometric study of Leu and Lin (1979). Garraway and Donovan (1980), using the flash photolysis - resonance absorption technique, reported that k varied from $(3.4 - 4.5) \times 10^{-12}$ $cm^3 molecules^{-1} s^{-1}$ as the total pressure increased from 10 - 240 torr ($M = SF_6$). Obviously, the results are not in particularly good agreement (a factor of 2.7 in the low pressure regime), but Garraway and Donovan only claimed a factor of two accuracy due to the complexity of their reaction system. A lower limit of 0.65 was determined by Leu and Lin for $k_1 (OH + ClO \rightarrow HO_2 + Cl)/k(OH + ClO \rightarrow$ products) at 298 K. The approach was somewhat indirect and the actual

value of k_1/k may possibly be unity. Garraway and Donovan have interpreted the observed pressure dependence in their study as being indicative of formation of an HOClO complex. Clearly additional studies of the rate constant and mechanism of this reaction as a function of pressure and temperature are required.

58. Unchanged from NASA 1049. These upper limits are based on the data of Walker (reported in Clyne and Watson (1974a)). The upper limits shown for k (298) were actually determined from data collected at either 587 K or 670 K. The Arrhenius expressions were estimated based on this $\sim$ 600 K data.

59. Unchanged from NASA 1049. The results reported by Clyne and Watson (1977) and Basco and Dogra (1971b) differ not only in the magnitude of the rate constants, but also in the interpretation of the reaction mechanism. The preferred value is that reported by Clyne and Watson. The temperature dependence for such processes is expected to be small, as for BrO + BrO. Although the second reaction channel is shown proceeding directly to Br + Cl + O_2, it may proceed through Br + ClOO (ΔH^O = -27.5 kJ mol^{-1}) or Cl + BrOO (ΔH^O unknown).

60. No recommendation at present. For a discussion of the ClO + ClO reactions the reader is referred to Watson (1977, 1980).

61. Unchanged from NASA 1049. The branching ratio between the two channels is not well-defined but, for the present discussion, is assumed to be unity. The Arrhenius expressions were estimated on the basis of data reported by DeMore, Lin and Jaffe (1976).

62. Unchanged from NASA 1049. Data reported by Bemand, Clyne and Watson (1973).

63. Unchanged from NASA 1049. Arrhenius expression was estimated based on 298 K data reported by Bemand, Clyne and Watson (1973).

64. Unchanged from NASA 1049. Arrhenius expression was estimated based on 298 K data reported by Bemand, Clyne and Watson (1973).

65. There have been several studies of each of the OH + $CH_xF_yX_{(4-x-y)}$ (X = Cl or Br) reactions, i.e. OH + CH_3Cl, CH_2Cl_2, $CHCl_3$, $CHFCl_2$, CHF_2Cl, CH_2ClF, and CH_3Br. In each case there has been quite good agreement between the reported results (except for Clyne and Holt, 1979b), both at $\sim$ 298 K and as a function of temperature. However, in certain cases it can be noted that the E/R values obtained from studies performed predominantly above 298 K were greater than the E/R values obtained from studies performed over a lower temperature range, e.g. the E/R value for OH + CH_3Cl reported by Perry et al. (1976a) is significantly higher than that reported by Davis et al. (1976). These small but significant differences could be attributed to either experimental error or non-linear Arrhenius behavior. The recent results of Jeong and Kaufman (1980) have shown a non-linear Arrhenius behavior for each reaction studied. They found that their data could best be represented by a three parameter equation of the form $AT^2\exp(-B/T)$. The experimental $AT^2\exp(-B/T)$ fit is stated by the authors to be in agreement with that expected from transition state theory.

The preferred values shown in this review were obtained by first fitting all of the absolute rate data for each reaction (except Clyne and Holt (1976b) to the three parameter equation $AT^2\exp(-B/T)$, and then simplifying these equations to a set of "derived Arrhenius expressions" centered at 265 K. The derived Arrhenius expressions were centered at 265 K as a temperature representatives of the mid-troposphere. The $AT^2\exp(-B/T)$ expressions are given for each reaction in the individual notes, while the "derived Arrhenius expressions" are entered in the table of

preferred values. Obviously "derived" Arrhenius expressions can be centered at any temperature from the three parameter equations (these should be restricted to within the temperature range studied). Transforming $k = AT^2\exp(-B/T)$ to the form $k = A^1\exp(-E/T)$: $E^1 = B + 2T$ and $A^1 = A \times e^2 \times T^2$.
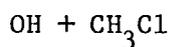
OH + CH$_3$Cl

Changed from NASA 1049. The preferred values were obtained using only absolute rate coefficient data. The studies which determined $k(\text{OH+CO})/k(\text{OH+CH}_3\text{Cl})$, (Davis et al. (1975), and Butler et al. (1978)), are excluded until the kinetic behavior between OH and CO is better understood, and the accuracy of the OH + CH$_4$: OH +CH$_3$Cl study (Cox et al. (1976a)) was probably no better than a factor of 2. The data of Howard and Evenson (1976a), Davis et al. (1976), Perry et al. (1976), and Jeong and Kaufman (1980) are in good agreement and was used to determined the preferred values. Fitting the data to an expression of the form $AT^2\exp(-B/T)$ results in the equation 3.49×10^{-18} $T^2\exp(-582/T)$ over the temperature range (247-483)K. This results in a preferred value of 4.40×10^{-14} cm^3 molecule^{-1} s^{-1} for k at 298K. The derived Arrhenius expression centered at 265K is $1.81 \times 10^{-12}\exp(-1112/T)$.
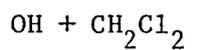
OH + CH$_2$Cl$_2$

Changed from NASA 1049. The preferred values were obtained using only absolute rate coefficient data. The accuracy of the OH + CH$_4$: OH +CH$_2$Cl$_2$ study (Cox et al. 1976a)) was probably no better than a factor of 2. The data of Howard and Evenson (1976a), Davis et al. (1976), Perry et al. (1976a), and Jeong and Kaufman (1980) are in good agreement and were used

to determine the preferred value (the values of Davis et al. are somewhat

lower (20%) than those reported in the other studies but are included in

the evaluation). Fitting the data to an expression of the form $AT^2\exp(-B/T)$

results in the equation $8.58 \times 10^{-18}\ T^2\exp(-502/T)$ over the temperature

range 245-455 K. This results in a preferred value of $1.41 \times 10^{-13}\ cm^3$

$molecule^{-1}\ s^{-1}$ for k at 298K. The derived Arrhenius expression centered

at 265K is $4.45 \times 10^{-12}\exp(-1032/T)$.
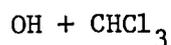
$OH + CHCl_3$

Changed from NASA 1049. The preferred values were obtained using only

absolute rate coefficient data. The accuracy of the $OH + CH_4$: $OH + CHCl_3$

study (Cox et al. (1976a)) was probably no better than a factor of 2. The

data of Howard and Evenson (1976a), Davis et al. (1976) and Jeong and

Kaufman (1980) were in good agreement and was used to determine the pre-

ferred values. Fitting the data to an expression of the form $AT^2\exp(-B/T)$

results in the equation $6.3 \times 10^{-18}\exp(-504/T)$ over the temperature range

245-487K. This results in a preferred value of $1.03 \times 10^{-13}\ cm^3\ molecule^{-1}$

s^{-1} for k at 298K. The derived Arrhenius expression centered at 265K is

$3.27 \times 10^{-12}\exp(-1034/T)$.
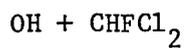
$OH + CHFCl_2$

Changed from NASA 1049. The preferred values were derived using the abso-

lute rate coefficient data reported by Howard and Evenson (1976a), Perry

et al. (1976a), Watson et al. (1977), Chang and Kaufman (1977), and Jeong and

Kaufman (1980). The data of Clyne and Holt (1979b) was not considered

as it is in rather poor agreement with the other data within the temperature

range studied, e.g. there is a difference of $\sim$ 65% at 400K. Fitting the data

to an expression of the form $AT^2\exp(-B/T)$ results in the equation 1.71×10^{-18}

$T^2 \exp(-483/T)$ over the temperature range 241-483K. This results in a pre-ferred value of 3.0×10^{-14} cm^3 molecule^{-1} s^{-1} for k at 298K. The derived Arrhenius expression centered at 265K is $0.89 \times 10^{-12} \exp(-1013/T)$.
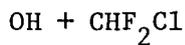
OH + CHF_2Cl

Changed from NASA 1049. The preferred values were derived using the absolute rate coefficient data reported by Howard and Evenson (1976a), Atkinson et al. (1975), Watson et al. (1977), Chang and Kaufman (1977), Handwerk and Zellner (1978), and Jeong and Kaufman (1980) which was in good agreement. The data of Clyne and Holt (1979b) was not considered as it is in rather poor agreement with the other data within the temperature range studied, except at 298K (the reported A-factor of $\sim 1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} is clearly inconsistent with that expected theoretically). Fitting the data to an expression of the form $AT^2 \exp(-B/T)$ results in the equation 1.51×10^{-18} $T^2 \exp(-1000/T)$ over the temperature range 250-482K. This results in a preferred value of 4.68×10^{-15} cm^3 molecule^{-1} s^{-1} for k at 298K. The derived Arrhenius expression centered at 265K is $0.78 \times 10^{-12} \exp(-1530/T)$.
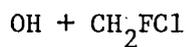
OH + CH_2FCl

Changed from NASA 1049. The preferred values were derived using the absolute rate coefficient data reported by Howard and Evenson (1976a), Watson et al. (1977), Handwerk and Zellner (1978), and Jeong and Kaufman (1980) which is in fair agreement. Fitting the data to an expression of the form $AT^2 \exp(-B/T)$ results in the equation 3.77×10^{-18} $T^2 \exp(-604/T)$ over the temperature range 245-486K. This results in a preferred value of 4.41×10^{-14} cm^3 molecule^{-1} s^{-1} for k at 298K. The derived Arrhenius expression centered at 265K is $1.96 \times 10^{-12} \exp(-1134/T)$.

66. Unchanged from NASA 1049. This evaluation is based on the recent data of Jeong and Kaufman (1979) and Kurylo et al. (1979). Their results are in excellent agreement over the temperature range 250-460K. The earlier results of Howard and Evenson (1976b), Watson et al. (1977), Chang and Kaufman (1977) and Clyne and Holt (1979a) are rejected in favor of the recent results. The earlier results showed higher values of the rate constant, and lower E/R values. This is indicative of the CH_3CCl_3 used in the early studies being contaminated with small amounts of a reactive olefinic impurity.

67. Unchanged from NASA 1049. The preferred value at 298K is a mean of the values reported by Howard (1976), Chang and Kaufman (1977) and Davis et al. (1978). As these values are in excellent agreement (better than 10%), the value reported by Winer et al. (1976) which is more than a factor of 10 greater must be rejected. The results of the temperature dependence studies reported by Chang and Kaufman, and Davis et al. are in excellent agreement (better than 30% at all temperatures between 220 and 425K). The preferred Arrhenius parameters are those of Chang and Kaufman as the data of Davis et al. has yet to be published.

68. Unchanged from NASA 1049. The results of the three absolute rate coefficient studies (Howard (1976), Chang and Kaufman (1977), and Davis et al. (1978)) are in excellent agreement at 298K. The value derived from a relative rate coefficient study by Winer et al (1976) is a factor of ~ 2 greater than the other values and is not considered in deriving the preferred value at 298K. The Arrhenius parameters are those reported by Chang and Kaufman.

69. Unchanged from NASA 1049. The A-factor was estimated, and a lower limit derived for E/R by using the upper limits reported for the rate constants

by Chang and Kaufman (1977) at ~ 480 K. These expressions are quite compatible with the upper limits reported for these rate constants by Atkinson et al. (1975), Howard and Evenson (1976a), Cox et al. (1976a) and Clyne and Holt (1979b). None of the investigators reported any evidence for reaction between OH and these chlorofluoromethanes.

70. Unchanged from NASA 1049. The results reported for k (298 K) by Clyne and Watson (1975), Leu and DeMore (1977), Michael et al. (1978) and Michael and Payne (1979) are in excellent agreement. The preferred value at 298 K is derived by taking a simple mean of these four values. The temperature dependences reported for k by Leu and DeMore, Michael et al. and Michael and Payne can only be considered to be in fair agreement. There is a spread of 25% in k at 220 K and 50% at 360 K. Although the results reported by Michael et al. and Michael and Payne are in good agreement, there is no reason at present to discard the results of Leu and DeMore. Therefore, until further results are reported, the preferred value was synthesized to best fit all the data reported from these four studies.

71. Unchanged from NASA 1049. The preferred value is based on the value reported by Clyne et al. (1976). This value appears to be quite reasonable in light of the known reactivity of ClO radicals with atomic oxygen. The temperature dependence of k is expected to be small for such an atom-radical process, e.g., O + ClO.

72. Unchanged from NASA 1049. The results of the three low pressure mass spectrometric studies (Clyne and Watson (1975), Ray and Watson (1980) and Leu (1979) and the high pressure uv absorption study (Watson et al. (1979)), which all used pseudo first-order conditions, are in excellent agreement at 298 K, and are thought to be much more reliable than the earlier low

pressure uv absorption study (Clyne and Cruse (1970b)). The results of the two

temperature dependence studies are in good agreement and both show a small

negative temperature dependence. The preferred Arrhenius expression was

derived from a least squares fit to all the data reported in the four

recent studies. By combining the data reported by Watson and Sander with

that from the three mass spectrometric studies, it can be shown that this

reaction does not exhibit any observable pressure dependence between 1 and

700 torr total pressure. The temperature dependence of k for the analogous

ClO and HO_2 reactions are also negative, and are similar in magnitude.

73. Unchanged from NASA 1049. Four of the five studies (Clyne and Coxon (1968),

Clyne and Cruse (1970a), Basco and Dogra (1971), and Sander and Watson

(1980), monitored the BrO radical concentration using ultraviolet absorption

spectrometry. As the reaction being studied was second order in [BrO]

knowledge of σ was required in order to determine k. There is substantial

disagreement between the values of σ. Although the magnitude of σ is

dependent upon the particular transition, and instrumental parameters such

as spectral bandwidth, the most probable reason for the differences is

that the techniques (based on reaction stoichiometries) used to determine

σ in the early studies (Clyne and Coxon, Clyne and Cruse, and Basco and

Dogra) were used incorrectly (discussed by Clyne and Watson (1975)). The

most recent study (Sander and Watson (1980)) used the same technique to

determine σ, but avoided the problems. In three of the studies (Clyne and

Coxon, Basco and Dogra, and Sander and Watson) there is good agreement in

the reported values of k/σ; however, this may be somewhat fortuitous as

σ is expected to vary somewhat from study to study. The preferred value

for k at 298 K is taken to be an average of the values reported by Clyne

and Watson (the mass spectrometric study where knowledge of σ is not

required) and Sander and Watson (the recent absorption study). There was

no observable pressure dependence (50-600 torr) in the recent flash photo-

lysis study. From the values of k reported by Clyne and Watson and Sander

and Watson, it can be stated that the BrO + BrO reaction exhibits no pres-

sure dependence within the range 1-600 torr. The recent flash photolysis

study determined the temperature dependence of both k/σ and σ independently.

The preferred Arrhenius expression uses the temperature dependence reported

by Sander and Watson, and the pre-exponential A-factor was adjusted to

yield the preferred value at 298 K. Although the partitioning of the total

rate constant into its two components, k_1 and k_2, was quantitatively

studied at 298 K by Sander and Watson, and the ratio $k_1/(k_1 + k_2)$ reported

to be 0.85 ± .05, it is not clear whether this ratio would be expected to

exhibit a temperature dependence (the values shown in the table assume

the partitioning is invariant with temperature). Whereas the ratio of

k_1/k_2 reported by Sander and Watson is in good agreement with that estimated

by Cruse (1971), the temperature dependence of $k_1 + k_2$ disagrees.

74. Unchanged from NASA 1049. Based on a study reported by Sander and Watson

(1980). Clyne and Cruse (1970a) also reported an upper limit of 8×10^{-14}

cm^3 molecule^{-1} s^{-1} for this reaction. Both studies reported that there is

no evidence for this reaction. The analogous ClO reaction has a rate

constant of $\sim 10^{-18}$ cm^3 molecule^{-1} s^{-1}.

75. Changed from NASA 1049. Using the discharge flow - mass spectrometric

technique Leu (1980), and Posey et al. (1980) determined an upper limit

for k of $\sim 1.5 \times 10^{-15}$ at ~ 298 K. Leu also reported an upper limit for

k of 3×10^{-15} at 417 K. An estimate of the Arrhenius expression would

be $< 1 \times 10^{-11}$ exp(-2650/T). The A-factor was chosen to be consistent

with that determined for the Cl + H_2O_2 reaction, and the E/R value was

calculated to yield the upper limit at 298 K.

76. Changed from NASA 1049. No recommendation until there is additional

experimental data. The NASA 1049 value was an estimate which assumed that

the reactivity of HO_2 with atomic chlorine and atomic bromine is similar.

Posey et al. (1980) used the discharge flow - mass spectrometric technique

to determine a value of 3×10^{-13} (± factor of 2) for k at 298 K. This

experimental value seems surprisingly low for an atom-radical reaction,

possibly suggesting experimental error. However, a preliminary value of

1.4×10^{-11} cm^3 $molecule^{-1}$ s^{-1} for k(Cl + HO_2) by Posey et al. (private

communication) is in fair agreement with the NASA preferred value.

Therefore, until there is an additional determination of this rate

constant it is suggested that a range of values $(1-500) \times 10^{-13}$ cm^3

$molecule^{-1}$ s^{-1} be used in any model calculations.

77. New entry. There have been two determinations of the rate constant at

298 K, which are not in good agreement. Le Bras et al. (1980) used the

discharge flow - EPR technique and reported a value of 1.6×10^{-12} cm^3

$molecule^{-1}$ s^{-1} while Nava et al. (1980) used the flash photolysis - resonance

fluorescence technique and reported a value of 1.08×10^{-12} cm^3 $molecule^{-1}$

s^{-1}. The preferred value is from the temperature dependent study of

Nava et al.

78. Unchanged from NASA 1049. Takacs and Glass (1973a) combined their results

with those of Wilson et al. (1969) and obtained the following Arrhenius

expression $(3.7 \pm 0.7) \times 10^{-11}$ exp$(-579 \pm 70)/T$. However, this expre-

sion is not recommended as the extrapolation is over too wide a

temperature range, and the value reported by Wilson et al. is questionable.
The values reported for k (298 K) by Takacs and Glass, and Ravishankara
et al. (1979a) differ by a factor of 2.4; therefore, until another study
is performed the preferred value should be taken to be a simple mean of
these values. The data reported by Ravishankara et al. shows that the
rate constant exhibits no temperature dependence between 249-416 K.
This observation is compatible with the estimated pre-exponential
A-factor being comparable to the value of k at 298 K.

79. Unchanged from NASA 1049. As the values reported for k at 298 K (Takacs
and Glass (1973b), Brown and Smith (1975) and Singleton and Cvetanovic
(1978)) are in fair agreement, the mean is taken to be the preferred
value. The agreement between the values deduced from the reported
Arrhenius expressions at stratospheric temperatures is rather poor, e.g.,
the values differ by ∿ 70% at 250 K. The preferred value has been
synthesized to best fit both sets of data between 250 and 400 K. The
A-factor derived for the preferred expression and that reported by
Brown and Smith appear to be lower than would be expected. This,
combined with the absence of data at stratospheric temperatures, leads
to considerable uncertainty in the values of k between 200 and 260 K.

80. Unchanged from NASA 1049. Value chosen to be comparable with the
value of $k(ClO + HO_2)$ at 298 K as there is no experimental data. The
uncertainty factor in k at 298 K precludes the need to estimate the
temperature dependence in k, as it would have a smaller magnitude,
than the uncertainty over the temperature range of the stratosphere.

81. Unchanged from NASA 1049. Value chosen to be consistent with
k(ClO + OH) due to the absence of any experimental data.

82. Changed from NASA 1049. The absolute rate coefficients determined by
Howard and Evenson (1976a) and Davis et al. (1976) are in excellent
agreement at 298 K. The same approach has been used to determine the

preferred Arrhenius parameters as was used for the OH + $CH_xF_yCl_{4-x-y}$

reactions. Fitting the data to an expression of the form $AT^2 \exp(-B/T)$

results in the equation $1.17 \times 10^{-18} T^2 \exp(-295/T)$ over the temperature

range 244-350 K. This results in a preferred value of 3.86×10^{-14} cm^3

$molecule^{-1} s^{-1}$ for k at 298 K. The derived Arrhenius expression

centered at 265 K is $6.09 \times 10^{-13} \exp(-825/T)$.

83. Unchanged from NASA 1049. The only experimental data is that reported

by Wagner et al. (1972). Value appears to be quite reasonable in view

of the well known reactivity of atomic chlorine with O_3.

84. Unchanged from NASA 1049. The value of k at $\sim$ 298 K seems to be fairly

well established with the results of Homan et al. (1970), Dodonov et al.

(1971), Clyne et al. (1973), Bozzelli (1973), and Igoshin et al. (1974)

being in excellent agreement considering the diverse nature of the

experimental techniques used. The value reported by Kompa and Wanner

(1972) appears to be too high by a factor of $\sim$ 2.5, whereas the values

reported by Rabideau et al. (1972) and Lam et al. (1974) are too low

by factors of 4 and 10, respectively. Therefore, the preferred value at

298 K is taken to be a mean of the five studies which are in good

agreement. However, the magnitude of the temperature dependence cannot

be considered to be well established with values of E/R of 805 (Homann

et al.) and 544 (Igoshin et al.) being reported. The preferred

Arrhenius parameters were derived by calculating A to be 2×10^{-10},

and calculating an E/R value to yield a value of 2.5×10^{-11} at 298 K.

For detailed comments refer to reviews by Jones and Skolnik (1976) and

Foon and Kaufman (1975). A-factor seems high.

85. Unchanged from NASA 1049. The three absolute rate coefficients determined

by Wagner et al. (1971), Clyne et al. (1973) and Kompa and Wanner (1972)

at 298 K are in good agreement; however, this may be somewhat fortuitous

as the ratios of $k(F + H_2)/k(F + CH_4)$ determined by these same groups can only be considered to be in fair agreement, 0.23, 0.42 and 0.88. The values determined for k (298) from the relative rate coefficient studies are also in good agreement with those determined in the absolute rate coefficient studies, and the value of 0.42 reported for $k(F + H_2)/k(F + CH_4)$ by Foon and Reid (1971) is in good agreement with that reported by Clyne et al. The preferred value of 8.0×10^{-11} for k (298) is a weighted mean of all the results. The magnitude of the temperature dependence is somewhat uncertain. The preferred Arrhenius parameters are based on the data reported by Wagner et al., and Foon and Reid, and the preferred Arrhenius parameters of the $F + H_2$ reaction. This reaction has recently been reviewed by both Foon and Kaufman (1975) and Jones and Skolnik (1976). A-factor may be too high.

86. Unchanged from NASA 1049. This is the value of Zetsch (1971) which was reported in the review of Jones and Skolnik (1976). The reactivity appears to be somewhat lower than might be expected for such a hydrogen abstraction reaction (see review of Foon and Kaufman (1975).

87. Unchanged from NASA 1049. This estimate is probably accurate to within a factor of 3, and is based upon the assumption that the reactivity of FO is similar to that of ClO and BrO. The experimentally determined rate constants for ClO and BrO at $\sim$ 298 K are 5.0×10^{-11} and 3.0×10^{-11}, respectively (NASA preferred values). The temperature dependence of the rate constant is expected to be small. The temperature dependence of the analogous ClO reaction has been studied twice with somewhat different results. The values reported for E/R are -76 K (Zahniser and Kaufman (1977) and +224 K Clyne and Nip (1976b)).

88. Changed from NASA 1049. Ray and Watson (1980) determined a value of 2.6×10^{-11} cm^3 $molecule^{-1}$ s^{-1} for k at 298 K using the discharge

flow-mass spectrometric technique. This value is almost identical to that estimated in NASA 1049 which was based on the assumption that the reactivity of NO and ClO and BrO would be similar. The temperature dependence of k is expected to be small for such a radical-radical reaction. The temperature dependences of k for the analogous ClO and BrO reactions have been reported to be negative with E/R values of -283 K and -265 K, respectively (NASA preferred values).

89. Unchanged from NASA 1049. Although the value of k (FO + FO) reported by Clyne and Watson (1974b) was obtained in a more direct manner than that of Wagner et al. (1972), and as such is less susceptible to error due to the presence of complicating secondary reactions and thus would normally be preferred, the value to be recommended in this assessment is a weighted average of the two studies. From the data of Wagner et al. it can be seen that the dominant reaction channel is that producing $2F + O_2$. However, their data base is not adequate to conclude that it is the only process.

90. Unchanged from NASA 1049. The $FO + O_3$ reaction has two possible pathways which are exothermic, resulting in the production of $F + 2 O_2$ or $FO_2 + O_2$. Although this reaction has not been studied in a simple direct manner, two studies of complex chemical systems have inferred some kinetic information about it. Starrico et al. (1962) measured quantum yields for ozone destruction in F_2/O_3 mixtures, and attributed the high values, $\sim$ 4600, to be due to the rapid regeneration of atomic fluorine via the $FO + O_3 \rightarrow F + 2 O_2$ reaction. However, their results are probably also consistent with the chain propagation process being $FO + FO \rightarrow 2 F + O_2$ (the latter reaction has been studied twice (Wagner et al. (1972), Clyne and Watson (1974b)), but although the value of $[F]_{produced}/[FO]_{consumed}$ is known to be close to unity, it has not been

accurately determined. Consequently it is impossible to ascertain from the experimental results of Starrico et al. whether or not the high quantum yields for ozone destruction should be attributed to the $FO + O_3$ reaction producing either $F + 2 O_2$ or $FO_2 + O_2$ (this process is also a chain propagation step if the resulting FO_2 radical preferentially reacts with ozone rather than with either FO or itself). Wagner et al. utilized a low pressure discharge flow-mass spectrometric system to study the $F + O_3$ and FO + FO reactions by directly monitoring the time history of the concentrations of F, FO and O_3. They concluded that the $FO + O_3$ reaction was unimportant in their system. However, their paper does not present enough information to warrant this conclusion. Indeed, their value of k(FO + FO) of 3×10^{-11} is about a factor of 4 greater than that reported by Clyne and Watson, which may possibly be attributed to either reactive impurities being present in their system, e.g., $O(^3P)$, or that the $FO + O_3$ reactions were not of negligible importance in their study. Consequently, it is not possible to determine a value for the $FO + O_3$ reaction rate constant from existing experimental data. It is worth noting that the analogous $ClO + O_3$ reactions are extremely slow ($\sim 10^{-18}$ cm^3 $molecule^{-1}$ s^{-1}) (DeMore et al. (1976)), and upper limits of 8×10^{-14} (Clyne and Cruse (1970a)) and 5×10^{-15} cm^3 $molecule^{-1}$ s^{-1} (Sander and Watson (1980)) have been reported for $BrO + O_3$.

91. Unchanged from NASA 1049. No experimental data. The rate constant for such a radical-atom process is expected to approach the gas collision frequency, and is not expected to exhibit a strong temperature dependence.

92. Unchanged from NASA 1049. No experimental data. k is assumed to be comparable to most other O^1D rate constants which approach the gas kinetic collision frequency, and as such is not expected to exhibit a strong temperature dependence.

93. The question of any contribution at stratospheric temperatures from

a bimolecular reaction has been considered in the past but dismissed,

based mainly on the observation by Baldwin and Golden (1978) that

$k < 5 \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1} for temperatures up to 1220 K. Two

very different recent reports confirm this. Klais et al. (1979)

obtained an upper limit at 368 K of $k < 3 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1}.

This was based on an attempt to detect OH attributable to the reaction

$CH_3 + O_2 \rightarrow OH + H_2CO$. A high temperature shock tube study by Bhasharan,

Frank and Just (1980) gives $k = 1 \times 10^{-11}$ $exp(-12,900/T)$ cm^3 $molecule^{-1}$

s^{-1} for the temperature range 1800-2200 K. Extrapolation to 1220 K

yields $k = 2.5 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1}.

94. The recommendation is based on the results of Washida and Bayes (1976)

obtained over the temperature range 259 to 341 K. Recent shock tube

results of Bhasharan, Frank and Just (1980) for the range 1600-2400 K

are compatible with the recommendation. This reaction is probably only

important in the vicinity of the stratopause.

95. The value for k (298 K) is the average of those determined by Sander

and Watson (1980a), Ravishankara et al. (1980), Plumb et al. (1979), and

Cox and Tyndall (1979,1980). Values lower by more than a factor of

two have been reported by Adachi and Basco (1979) and Simonaitis and

Heicklen (1979). Interference from formation of CH_3ONO very likely

occurred in the former direct study while the latter relative

determination is based on a value for $CH_3O_2 + SO_2$ which is at variance

with the recommendation given in these evaluations. It is not expected

that this reaction would have much of a temperature dependence and

Ravishankara et al. (1980) could find no evidence for any temperature

dependence within the error limits of their experiments (± 20%) over

the range 250 to 350 K. These authors also find that the reaction

channel leading to NO_2 formation accounts for at least 80% of the reaction.

96. The room-temperature value is that of Cox and Tyndall (1979,1980).
This study also reports a large negative E/R value over the temperature
range 274 to 338 K. This is similar to that found by this group for
HO_2 + HO_2. This requires independent verification, preferably over
a wide temperature range. More work is needed, especially on the
question of water vapor dependence.

97. This upper limit is based on the study of Sander and Watson (1980b).
Values for k (298 K) approximately two orders of magnitude larger
than this have been reported by Kan et al. (1979) and by Sanhueza
et al. (1979). However, considering the similarity of the reactivity
of HO_2 and CH_3O_2, it seems more reasonable that the reaction
CH_3O_2 + SO_2 would be negligibly slow at 298 K.

98. The recommended value for k (298 K) is the average of those reported
by Hochanadel et al. (1977), Parkes (1977), Anastasi et al. (1978),
Kan et al. (1979), Sanhueza et al. (1979) and Sander and Watson (1980a).
Because this reaction is second order in CH_3O_2, the absolute concentration
of the radical must be known. All the above determinations used
ultraviolet absorption techniques to determine $[CH_3O_2]$. The derived
k (298 K) values thus differ mostly due to differences in the CH_3O_2
absorption cross sections employed. The temperature range over which
the reaction has been studied is too small to allow for a recommendation
for the temperature dependence of the rate constant. The reaction
has three possible product channels: 2 CH_3O + O_2, CH_3OH + H_2CO + O_2,
and CH_3OOCH_3+ O_2. Although some studies have been made, the branching
ratios for these channels remain poorly defined. Thus further work is
required on both the temperature dependence and the branching ratio.

99. The recommended A-factor and E/R are the average of those determined by
Barker et al. (1977) and Batt and Robinson (1979). In both studies,
the ratio $k(CH_3 + O_2)/k(CH_3O + NO_2 + M)$ was measured over essentially

the same small temperature interval ($\sim$ 390 to 440 K). The k (298 K)

value is calculated from the recommended A-factor and E/R. Further

work is needed, preferably a direct study of the absolute rate constant

and over a wider temperature range.

100. The value for k(298 K) is the average of those determined by Atkinson

and Pitts (1978) and Stief et al. (1980), both using the flash

photolysis-resonance fluorescence technique. The value reported by

Morris and Niki (1971) agrees within the stated uncertainty. There

are two relative values which are not in agreement with the recommendations.

The value of Niki et al. (1978b) relative to OH + C_2H_4 is higher while

the value of Smith (1978) relative to OH + OH is lower. The latter

data are also at variance with the negligible temperature dependence

observed in the two flash photolysis studies. Although Atkinson and

Pitts assign a small energy barrier (E/R = 90 + 150), their data at

356 K and 426 K and that of Stief et al. at 228 K, 257K and 362 K are

all within 10% of the k(298 K) value. Thus, the combined data set

suggest E/R = 0. The abstraction reaction given is probably the major

channel; other channels may contribute (Horowitz et al., 1978).

101. The recommended values for A, E/R and k(298 K) are the averages of

those determined by Klemm (1979) using flash photolysis-resonance

fluorescence (250 to 498 K); by Klemm et al. (1980) using discharge

flow-resonance fluorescence (298 to 748 K); and Chang and Barker

(1979) using discharge flow-mass spectrometry (296 to 436 K). All

three studies are in good agreement. The k(298 K) value is also

consistent with the results of Niki et al. (1969), Herron and

Penzhorn (1969), and Mack and Thrush (1973). Although the mechanism

for O + H_2CO has been considered to be the abstraction reaction

yielding OH + HCO, Chang and Barker suggest that an addition channel

yielding H + HCO_2 may be occurring to the extent of 30% of the total

reaction. This conclusion is based on an observation of CO_2 as a

product of the reaction under conditions where reactions such as

$O + HCO \rightarrow H + CO_2$ and $O + HCO \rightarrow OH + CO$ apparently do not occur.

This interesting suggestion needs independent confirmation.

102. The value for k(298 K) is the average of the determinations by

Washida et al. (1974), Shibuya et al. (1977) and Clark et al. (1978).

103. This estimate is based on an assumed similarity to $OH + H_2O_2$ and

$OH + CH_3OH$. The k(298 K) values for these two reactions are reported

to be similar: $k(OH + H_2O_2) = 1.7 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} (this

evaluation) and $k(OH + CH_3OH) = 9.5 \times 10^{-13}$ $molecule^{-1}$ s^{-1} (Campbell

et al., 1976). In the absence of temperature-dependent data for

$OH + CH_3OH$, the E/R value is assumed to be the same as that for

$OH + H_2O_2$. The reaction products are not specified since, using

the above analogies to CH_3OH and H_2O_2, abstraction of H from either

end of the molecule may be equally probable.

104. This recommendation accepts the recent determination by Singleton

et al. (1979). The uncertainty factor in k(298 K) was chosen to

encompass the values of k(298 K) determined by Hollinden et al. (1970);

Whytock et al. (1976); and Slagle et al. (1978). The E/R value is that

of the Singleton study as confirmed by the higher temperature data of

Whytock et al., and the measurements of Slagle et al. It should be

emphasized that the Singleton determination did not extend below 298 K.

The only existing data below 298 K appear to indicate a dramatic change

in E/R in this temperature region. Thus ΔE/R was set to account for

these observations. Such a nonlinearity in the Arrhenius plot might

indicate a change in reaction mechanism from abstraction (as written)

to addition. An addition channel has been proposed for $O + H_2S$ by

Slagle et al. (1978) as well as by Singleton et al., and addition
products from this reaction have been seen in a matrix (Smardzewski
and Lin, 1977). Further kinetic study is recommended in the 200 to
300 K range. Direct mechanistic information is needed.

105. The value for k(298 K) is the average of five different studies of
this reaction: Westenberg and de Haas (1969), Klemm and Stief (1974),
Wei and Timmons (1975), Manning et al. (1976) and Breckenridge and
Miller (1972). The recommended value for E/R is the average of those
determined in the temperature studies reported in the first three
references. Hsu et al. (1979) report that this reaction proceeds
exclusively by a stripping mechanism.

106. The value of k(298 K) is the average of six determinations: Wei and
Timmons (1975), Westenberg and de Haas (1969), Slagle et al. (1974),
Callear and Smith (1967), Callear and Hedges (1970) and Homann et al.
(1968). The E/R value is that of Wei and Timmons (1975). Δ E/R has
been set to encompass within a 2 σ error band the limited temperature
data of Westenberg and de Haas (1969). Hsu et al. (1979) report that
1.4% of the reaction proceeds through the channel yielding CO + S_2
and calculate a rate constant for the overall process in agreement
with that recommended.

107. The recommended values for k(298 K) and E/R are the average values
determined by Westenberg and de Haas (1973b) and Perry et al. (1976b).
The recent relative value of Cox and Shepard (1980) is consistent with
the recommendation. Δ log k has been chosen to encompass the lower
value of Stuhl (1974) within the 2 σ error band. Δ E/R was chosen to
encompass both the 440 value of Westenberg and de Haas (1973b) and
the zero value of Perry et al. (1976b). Very recent results by Leu and
Smith at JPL (private communication, 1980) and by Michael et al. at

GSFC (private communication, 1980) are in reasonable agreement with each other and suggest a somewhat lower k(298 K) value as well as E/R closer to that of Perry et al. (1976b). When these results are available in final form, a revised recommendation will be made.

108. This upper limit is based on the recent study by Ravishankara et al. (1980). Their observations point to the possibility of complications due to secondary chemistry and/or excited state reactions in the studies of Atkinson et al. (1978) and Kurylo (1978). Measurements by Ravishankara et al. above 298 K can be used to calculate an E/R value of 2450 K. Their upper limit is consistent with the upper limit reported by Cox and Sheppard (1980). Separate confirmation of these limiting values would be helpful.

109. This upper limit is based on the recent study by Wine et al. (1980b). These authors dealt with severe complications due to excited state and secondary chemistry. The extremes in experimental variation which were necessary to minimize these effects indicate remaining complications in the studies of Atkinson et al. (1978), Kurylo (1978) and Cox and Sheppard (1980). This interpretation is consistent with an upper limit for the rate of production of OCS in the OH + CS_2 reaction system reported by Iyer and Rowland (1980).

Table 2. Rate Constants for Three-Body Reactions.

Reaction	Low Pressure Limit $k_o(T) = k_o^{300}(T/300)^{-n}$		High Pressure Limit $k_\infty(T) = k_\infty^{300}(T/300)^{-m}$		Notes
	k_o^{300}	n	k_∞^{300}	m	
*$HO_2 + NO_2 \overset{M}{\to} HO_2NO_2$	$(2.1 \pm 0.4)(-31)$	5.0 ± 2.0	$(6.5 \pm 3.3)(-12)$	2.0 ± 2.0	1
$OH + NO_2 \overset{M}{\to} HNO_3$	$(2.6 \pm 0.3)(-30)$	2.9 ± 0.7	$(2.4 \pm 1.2)(-11)$	1.3 ± 1.0	2
$ClO + NO_2 \overset{M}{\to} ClONO_2$	$(1.6 \pm 0.2)(-31)$	3.4 ± 0.3	$(1.5 \pm 0.7)(-11)$	1.9 ± 1.0	3
(Two recommendations)	$(3.5 \pm 1.7)(-32)$	3.8 ± 1.0	$(1.5 \pm 0.7)(-11)$	1.9 ± 1.0	
$CH_3 + O_2 \overset{M}{\to} CH_3O_2$	$(2.2 \pm 1.1)(-31)$	2.2 ± 1.0	$(2.0 \pm 1.0)(-12)$	1.7 ± 1.0	4
$O + O_2 \overset{M}{\to} O_3$	$(6.2 \pm 0.9)(-34)$	2.0 ± 0.5	–	–	5
$O(^1D) + N_2 \overset{M}{\to} N_2O$	$(3.5 \pm 3.0)(-37)$	$0.45^{+2.0}_{-.45}$	–	–	6
$Cl + NO \overset{M}{\to} ClNO$	$(9.0 \pm 2.0)(-32)$	1.8 ± 0.5	–	–	7
$Cl + NO_2 \overset{M}{\to} ClNO_2$ (ClONO)	$(1.6 \pm 1.0)(-30)$	1.9 ± 1.0	$(3.0 \pm 1.5)(-11)$	1.0 ± 1.0	8
$Cl + O_2 \overset{M}{\to} ClOO$	$(2.0 \pm 1.0)(-33)$	$1.3^{+2.0}_{-1.3}$	–	–	9
$H + O_2 \overset{M}{\to} HO_2$	$(5.5 \pm 0.5)(-32)$	1.4 ± 0.5	–	–	10
$OH + NO \overset{M}{\to} HONO$	$(6.7 \pm 1.2)(-31)$	3.3 ± 1.0	$(3.0 \pm 1.5)(-11)$	1.0 ± 1.0	11
$F + O_2 \overset{M}{\to} FO_2$	$(1.1 \pm 0.3)(-32)$	1.7 ± 1.0	–	–	12
$OH + OH \overset{M}{\to} H_2O_2$	$(2.5 \pm 1.3)(-31)$	$0.8^{+2.0}_{-0.8}$	$(3.0 \pm 1.5)(-11)$	1.0 ± 1.0	13
*$CH_3O_2 + NO_2 \overset{M}{\to} CH_3O_2NO_2$	$(1.5 \pm 0.8)(-30)$	4.0 ± 2.0	$(6.5 \pm 3.2)(-12)$	2.0 ± 2.0	14
$F + NO \overset{M}{\to} FNO$	$(6.6 \pm 3.3)(-32)$	$1.0^{+2.0}_{-1.0}$	–	–	15
$FO + NO_2 \overset{M}{\to} FNO_3$	$(8.3 \pm 6.0)(-31)$	$0.7^{+3.0}_{-0.7}$	$(2.0 \pm 1.0)(-11)$	1.5 ± 1.5	16
$F + NO_2 \overset{M}{\to} FNO_2$ (FONO)	$(1.3 \pm 0.7)(-30)$	$1.7^{+2.0}_{-1.7}$	$(3.0 \pm 1.5)(-11)$	1.0 ± 1.0	17
*$BrO + NO_2 \overset{M}{\to} BrNO_3$	$(5.0 \pm 1.0)(-31)$	4.0 ± 2.0	–	–	18
*$NO_2 + NO_3 \overset{M}{\to} N_2O_5$	$(1.4 \pm 0.7)(-30)$	2.8 ± 1.0	$(8.0 \pm 4.0)(-13)$	0 ± 1.0	19
$O + NO \overset{M}{\to} NO_2$	$(1.2 \pm 0.3)(-31)$	1.8 ± 0.5	$(3.0 \pm 1.0)(-11)$	0 ± 1.0	20
$O + NO_2 \overset{M}{\to} NO_3$	$(9.0 \pm 1.0)(-32)$	2.0 ± 1.0	$(2.2 \pm 0.3)(-11)$	0 ± 1.0	20
$OH + SO_2 \overset{M}{\to} HOSO_2$	$(3.0 \pm 1.5)(-31)$	2.9 ± 1.0	$(2.0 \pm 1.5)(-12)$	0 ± 1.0	20

Note: $k(z) = k(M,T) = \left(\dfrac{k_o(T)[M]}{1 + k_o(T)[M]/k_\infty(T)} \right) 0.6^{\{1 + [\log_{10}(k_o(T)[M]/k_\infty(T))]^2\}^{-1}}$

(The values quoted are suitable for Air as the Third Body, M)

*Changed from NASA RP 1049.

Notes to Table 2

1. Low-pressure limit at 300 K from Howard (1977); T-dependence from computed

   strong collision rate constant (5.0×10^{-31}) and β_{N_2} value (0.42), which

   leads to $<\Delta E>_{N_2}$ = 0.81 kcal mole^{-1}. Assuming $<\Delta E>$ is temperature

   independent leads to k_o at 200 K = 1.6×10^{-30}, and hence the recommended

   n = 5. High-pressure limit at 300 K from RRKM model of Baldwin and

   Golden (1978); T-dependence from Baldwin and Golden (1978) and data over

   the range 254-283 K from Graham, Winer, and Pitts (1977).

2. Low-pressure limit from Anderson et al (1974), who report n = 2.5 (240

   < T/K < 450); Howard and Evenson (1974); Anastasi and Smith (1976), who

   report n = 2.6 (220 < T/K < 550) and Wine et al. (1979), who support these values

   over the range (247 < T/K < 352). The recommended value of n = 2.9 comes

   from $<\Delta E>_{N_2}$ = 0.31 kcal mole^{-1}. The high-pressure limit and T-dependence come

   from RRKM model of Smith and Golden (1978).

3. Values obtained by measuring the disappearance of reactants (Zahniser et

   al., 1977; Birks et al., 1977; and Leu et al., 1977) are about a factor

   of four higher than those obtained from the temperature dependence of the

   low-pressure limiting rate constant for the decomposition of $ClONO_2$,

   combined with an equilibrium constant calculated from ΔS = 40.6 eu,

   ΔH = 26.12 kcal mole^{-1}. It has been suggested that there are multiple

   pathways for the reaction of ClO with NO_2 (Knauth, 1978). Thus, we

   have made two different recommendations.

4. Low-pressure limit from extrapolation of data of Washida and Bayes (1976),

   Basco et al. (1972), and Parkes (1977). [The extrapolation techniques

   were poor, but this is not a very sensitive reaction.] Low-pressure limit

T-dependence as per text. High-pressure limit from van den Bergh and

Callear (1971) and Hochanadel et al. (1977). [Data of Basco et al. (1972),

Washida and Bayes (1976), Laufer and Bass (1975) is also considered.]

High-pressure limit T-dependence estimated.

5. Low-pressure limit and T-dependence from Klais, Anderson, and Kurylo (1980).

   In agreement with most earlier work (see references therein).

6. Low-pressure limit from Kajimoto and Cvetanovic (1976). T-dependence from

   same β value which is extremely low in this special system due to electronic

   curve crossing.

7. Low-pressure limit from Lee et al. (1978a), Clark et al. (1968), Ashmore

   and Spencer (1959), and Ravishankara, et al. (1978).

8. Low-pressure limit and T-dependence from Ravishankara et al. (1978) and

   Chang et al. (1978). The latter paper shows why Niki (1978a) saw two

   products with ClONO dominating (see note 3). $\beta = 0.37$ arrived at by

   dividing the sum of k_{sc} for 8a and 8b into measured rate constant for

   overall reaction of $Cl + NO_2$. High-pressure limit and temperature

   dependence are estimated.

9. Stedman et al. (1968) and Nicholas and Norrish (1968) measured this process

   in Ar. Recommended value based on $k(N_2)/k(Ar) \simeq 1.8$. T-dependence from

   constant $<\Delta E>$.

10. Kurylo (1972), Wong and Davis (1974) averaged. Both studies include

    T-dependence; the recommended value is chosen with constant $<\Delta E>_{N_2} \sim .04$

    kcal mole^{-1}. This very low number reflects rotational effects.

11. Anderson et al. (1974), Howard and Evensen (1974), Harris and Wayne (1975),

    measured the low-pressure limit. The T-dependence comes from Anderson

    et al. (1974), albeit in He. High-pressure limit and T-dependence are

    estimated.

12. Low-pressure limit from Baulch et al. (1980); T-dependence from constant

    $<\Delta E>$. (Baulch et al. (1980) recommend n = 2).

13. Zellner and Wagner (1980).

14. Parameters from a reasonable fit to the temperature and pressure-dependent data in Sander and Watson (1980) and Ravishankara et al. (1980), using equation (1).

15. Parameters estimated from strong collision calculations with β set at 0.3. T-dependence as per text.

16. Low-pressure limit from strong collision calculation and $\beta = 0.3$. T-dependence from constant $<\Delta E>$. High-pressure limit estimated to be same as reaction (3), including T-dependence. (Caveat: There could easily be multiple channels here as in reaction 3!)

17. For reaction (15a) the low-pressure limit rate constant is calculated from strong collisions and β 0.3. T-dependence from constant $<\Delta E>$. High-pressure limit estimated to be the same as reaction (8). Reaction 15b) might be the more important path; this calculation has not been attempted.

18. Values are from Sander et al. (1981). They report an extrapolated value of k_∞ as well, but we don't repeat that here since the extrapolation has many parameters. There may be multiple pathways as for reaction (3).

19. Data from Connell and Johnston (1979) and Viggiano et al. (1981).

20. Evaluation from Baulch et al. (1980).

PHOTOCHEMICAL DATA

Discussion of Format and Error Estimates

Presentation of photochemical cross sections is a more difficult problem than that of rate constant data, because of the large amount of data involved. In Table 3 we summarize the list of photochemical reactions considered to be of stratospheric interest. In cases where the data presentation is very complex, or where the reaction is of lesser importance, only a reference to a data source is given (see footnotes to the table). For example, discussion of the absorption cross sections of O_2 and O_3 - which largely determine the extent of penetration of solar radiation into the stratosphere and troposphere - are found in Hudson and Kieffer (1975) and NASA RP 1049. The photodissociation of NO in the O_2 Schumann-Runge band spectral range is another important process requiring special treatment; see Frederick and Hudson (1979). For the remainder of the entries, data are presented (for the most part) in the form of tables of cross sections vs. wavelengths.

Table 4 gives recommended reliability factors for some of the more important photochemical reactions. These factors generally refer to total dissociation rate regardless of product identity. The absorption cross sections are defined by the following expression of Beer's Law:

$$I = I_o \exp(-\sigma n l),$$

where: I_o, I are the incident and transmitted light intensity, respectively; σ is the absorption cross section in cm^2 molecule^{-1}; n is the concentration in molecule cm^{-3}; and l is the pathlength in cm. The cross sections are room temperature values unless otherwise stated.

Table 3.   Photochemical Reactions of Stratospheric Interest

$O_2 + h\nu \rightarrow O + O$	(1)	$HF + h\nu \rightarrow H + F$	(5)
$O_3 + h\nu \rightarrow O + O_2$	(1)	$HOCl + h\nu \rightarrow OH + Cl$	
$*O_3 + h\nu \rightarrow O(^1D) + O_2$		$HClO_4 + h\nu \rightarrow products$	(5)
$NO + h\nu \rightarrow N + O$	(2)	$ClNO + h\nu \rightarrow Cl + NO$	(7)
$NO_2 + h\nu \rightarrow NO + O$		$ClNO_2 + h\nu \rightarrow products$	(7)
$*NO_3 + h\nu \rightarrow products$		$ClONO + h\nu \rightarrow products$	(7)
$N_2O + h\nu \rightarrow N_2 + O(^1D)$		$ClONO_2 + h\nu \rightarrow products$	
$N_2O_5 + h\nu \rightarrow products$		$Cl_2 + h\nu \rightarrow Cl + Cl$	(6)
$NH_3 + h\nu \rightarrow NH_2 + H$	(1)	$Cl_2O + h\nu \rightarrow Cl + ClO$	(6)
$HO_2 + h\nu \rightarrow products$	(3)	$CCl_4 + h\nu \rightarrow products$	
$H_2O + h\nu \rightarrow H + OH$	(1)	$CCl_3F + h\nu \rightarrow products$	
$H_2O_2 + h\nu \rightarrow OH + OH$		$CCl_2F_2 + h\nu \rightarrow products$	
$HNO_2 + h\nu \rightarrow OH + NO$	(4)	$CClF_3 + h\nu \rightarrow products$	(7)
$HNO_3 + h\nu \rightarrow OH + NO_2$		$CHCl_2F + h\nu \rightarrow products$	(6)
$*HNO_4 + h\nu \rightarrow products$		$CHClF_2 + h\nu \rightarrow products$	
$SO_2 + h\nu \rightarrow SO + O$	(4)	$CH_2ClF + h\nu \rightarrow products$	(6)
$H_2S + h\nu \rightarrow HS + H$	(3)	$CH_3Cl + h\nu \rightarrow products$	
$CO + h\nu \rightarrow C + O$	(1)	$CCl_2FCClF_2 + h\nu \rightarrow products$	(7)
$CO_2 + h\nu \rightarrow CO + O$	(1)	$CClF_2CClF_2 + h\nu \rightarrow products$	(7)
$CH_4 + h\nu \rightarrow products$	(3)	$CClF_2CF_3 + h\nu \rightarrow products$	(7)
$CH_2O + h\nu \rightarrow products$		$*CH_3CCl_3 + h\nu \rightarrow products$	
$ClO + h\nu \rightarrow Cl + O$	(5)	$CCl_2O + h\nu \rightarrow products$	
$ClO_2 + h\nu \rightarrow products$	(6)	$CClFO + h\nu \rightarrow products$	
$OClO + h\nu \rightarrow O + ClO$	(6)	$CF_2O + h\nu \rightarrow products$	
$ClO_3 + h\nu \rightarrow products$	(7)	$CH_3OOH + h\nu \rightarrow products$	
$HCl + h\nu \rightarrow H + Cl$		$COS + h\nu \rightarrow CO + S$	(4)
		$BrONO_2 + h\nu \rightarrow products$	

* New data or comment.

(1) Hudson and Kieffer (1975)

(2) Frederick and Hudson (1979)

(3) Turco (1975)

(4) JPL Publication 79-27

(5) NASA RP 1049

(6) Watson (1977)

(7) NASA RP 1010

Table 4.   Reliability Estimates for Photochemical Rates

Species	Uncertainty Factor
O_2 (Schumann-Runge bands)	1.4
O_2 (Continua)	1.15
O_3	1.12
$O_3 \rightarrow O(^1D)$	1.4
NO_2	1.25
$NO_3 \rightarrow \begin{cases} NO + O_2 \\ NO_2 + O \end{cases}$	2.0
N_2O	1.2
N_2O_5	2.0
H_2O_2	1.4
HNO_3	1.15
HO_2NO_2	2.0
$CH_2O \rightarrow \begin{cases} H + HCO \\ H_2 + CO \end{cases}$	1.4
HCl	1.12
$HOCl$	1.4
$ClONO_2$	1.25
CCl_4	1.1
CCl_3F	1.05
CCl_2F_2	1.15
CH_3Cl	1.1
CF_2O	2.0
CH_3OOH	1.4
$BrONO_2$	1.4

$O_3 + h\nu \rightarrow O(^1D) + O_2$
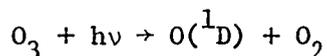
The quantum yields for $O(^1D)$ production, $\phi(O^1D)$, for wavelengths near 310 nm—i.e., the energetic threshold or fall-off region—have been measured mostly relative to quantum yields for wavelengths shorter than 300 nm, which were assumed to be unity. There are now several studies which indicate that this assumption is not correct: Fairchild et al. (1978) observed approximately 10% of the primary photolysis products in the ground state channel, that is, $\phi(O^3P) \simeq 0.1$, at 274 nm; Sparks et al. (1980) also report $\phi(O^3P) \simeq 0.1$, at 266 nm; according to Brock and Watson (1980b) $\phi(O^1D) = 0.88$ at 266 nm; and Amimoto et al. (1980) report $\phi(O^1D) = 0.85$ at 248 nm. There are also some indications that $\phi(O^1D)$ decreases slightly between 304 and 275 nm (see Brock and Watson, 1978 a, b).

Our previous recommendation for the quantum yields in the fall-off region was to employ the mathematical expression given by Moortgat and Kudzus (1978), which gives relative values in good agreement with those reported by Brock and Watson (1980a). Our present recommendation, shown in Table 5, merely scales down these values by a factor of 0.9 to account for the absolute magnitude of $\phi(O^1D)$ at short wavelengths.

Table 5. Mathematical Expression for $O(^1D)$ Quantum Yields, φ, in the Photolysis of O_3

$$\varphi(\lambda, T) = A(\tau) \arctan[B(\tau)(\lambda - \lambda_o(\tau))] + C(\tau)$$

Where: $\tau = T - 230$ is a temperature function with T given in Kelvin,

λ is expressed in nm, and arctan in radians.

The coefficients $A(\tau)$, $B(\tau)$, $\lambda_o(\tau)$ and $C(\tau)$ are expressed as interpolation polynomials of the third order:

$$A(\tau) = 0.332 + 2.565 \times 10^{-4} \tau + 1.152 \times 10^{-5} \tau^2 + 2.313 \times 10^{-8} \tau^3$$

$$B(\tau) = -0.575 + 5.59 \times 10^{-3} \tau - 1.439 \times 10^{-5} \tau^2 - 3.27 \times 10^{-8} \tau^3$$

$$\lambda_o(\tau) = 308.20 + 4.4871 \times 10^{-2} \tau + 6.9380 \times 10^{-5} \tau^2 - 2.5452 \times 10^{-6} \tau^3$$

$$C(\tau) = 0.466 + 8.883 \times 10^{-4} \tau - 3.546 \times 10^{-5} \tau^2 + 3.519 \times 10^{-7} \tau^3.$$

In the limits where $\varphi(\lambda, T) > 0.9$, the quantum yield is set $\varphi = 0.9$, and similarly for $\varphi(\lambda, T) < 0$, the quantum yield is set $\varphi = 0$.

$NO_2 + h\nu \rightarrow NO + O$
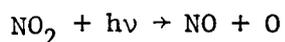
Table 6 lists the recommended absorption cross sections of nitrogen dioxide, taken from the work of Bass et al. (1976), who report extinction coefficients every 1/8 nm between 185 and 410 nm at 298K, and between 290 and 400 nm at 235K. The effect of the dimer (N_2O_4) absorption was considered in detail, and the measurements are probably correct to within ±10%.

Harker et al. (1977) have reported measurements of absorption cross sections and quantum yields in the 375-420 nm region. Their cross sections are 4-10% larger than the values reported by Bass et al. (1976), and their quantum yields are, on the average, about 15% smaller than those measured by Jones and Bayes (1973), whose data provided the basis for earlier recommendations. Recent measurements of the quantum yields by Davenport (1978) at six different wavelengths agree very well with those of Harker et al. The recommended values for the quantum yields, presented in Table 7, are those of Harker et al. (1977). Davenport's results indicate that the quantum yields themselves are temperature dependent, although the effect of temperature on the cross sections is more pronounced.

Table 6. NO_2 Absorption Cross Sections at 235 and 298 K

λ (nm)	$10^{20}\sigma(cm^2)$		λ (nm)	$10^{20}\sigma(cm^2)$	
	235 K	298 K		235 K	298 K
185		26.0	300	10.9	11.7
190		29.3	305	16.7	16.6
195		24.2	310	18.3	17.6
200		25.0	315	21.9	22.5
205		37.5	320	23.5	25.4
210		38.5	325	25.4	27.9
215		40.2	330	29.1	29.9
220		39.6	335	31.4	34.5
225		32.4	340	32.3	38.8
230		24.3	345	34.3	40.7
235		14.8	350	31.1	41.0
240		6.70	355	43.7	51.3
245		4.35	360	39.0	45.1
250		2.83	365	53.7	57.8
255		1.45	370	48.7	54.2
260		1.90	375	50.0	53.5
265		2.05	380	59.3	59.9
270		3.13	385	57.9	59.4
275		4.02	390	54.9	60.0
280		5.54	395	56.2	58.9
285		6.99	400	66.6	67.6
290	6.77	8.18	405	59.6	63.2
295	8.52	9.67	410	53.2	57.7

Table 7.   Quantum Yields for NO_2 Photolysis

λ,nm	Φ	λ,nm	Φ	λ,nm	Φ
375	0.73	389	0.74	400	0.65
376	0.75	390	0.74	401	0.62
377	0.86	391	0.81	402	0.57
378	0.74	392	0.73	403	0.50
379	0.83	393	0.78	404	0.40
380	0.81	394	0.83	405	0.32
381	0.73	394.5	0.78	406	0.30
382	0.65	395	0.81	407	0.23
383	0.62	395.5	0.75	408	0.18
384	0.66	396	0.78	409	0.17
385	0.70	396.5	0.81	410	0.14
386	0.74	397	0.77	411	0.10
387	0.69	398	0.72	415	0.067
388	0.76	399	0.70	420	0.023

$NO_3 + h\nu \rightarrow NO + O_2$

$NO_3 + h\nu \rightarrow NO_2 + O$
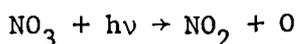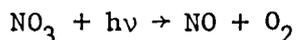
Magnotta and Johnston (1980) have studied the photolysis of the nitrate free radical using a pulsed laser technique, and their results supersede the earlier work of Graham and Johnston (1978). The recommendation is to use the following photodissociation rates estimated by Magnotta and Johnston (1980) for overhead sun at the earth's surface:

$$J_1(NO + O_2) = 0.022 \ s^{-1}.$$
$$J_2(NO_2 + O) = 0.18 \ s^{-1}.$$

$N_2O + h\nu \rightarrow N_2 + O(^1D)$
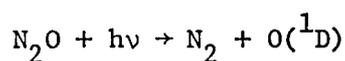
The recommended values are taken from the work of Selwyn et al. (1977), who measured the temperature dependence of the absorption cross sections in the atmospherically relevant wavelength region. They have fitted their data with the expression shown in Table 8.

Table 8.   Mathematical Expression for Absorption Cross Sections of N_2O as a Function of Temperature

$\ell n \ \sigma(\lambda,T) = A_1 + A_2\lambda + A_3\lambda^2 + A_4\lambda^3 + A_5\lambda^4$
$\qquad\qquad + (T-300)\exp(B_1 + B_2\lambda + B_3\lambda^2 + B_4\lambda^3)$

Where: T: temperature, Kelvin λ: nm

$A_1 = 68.21023$ $B_1 = 123.4014$

$A_2 = -4.071805$ $B_2 = -2.116255$

$A_3 = 4.301146 \times 10^{-2}$ $B_3 = 1.111572 \times 10^{-2}$

$A_4 = -1.777846 \times 10^{-4}$ $B_4 = -1.881058 \times 10^{-5}$

$A_5 = 2.520672 \times 10^{-7}$

Range: 173 to 240 nm; 194 to 320K

N_2O_5 + hν → products
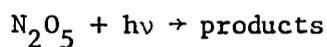
Table 9 lists data for N_2O_5 taken from Graham (1975) (see also Graham and Johnston, 1978), which supersede the results from the review article by Johnston and Graham (1974). The quantum yields for photodissociation are unknown; possible products are NO_2 + NO_3 and N_2O_4 + O.

Table 9.   Absorption Cross Sections of N_2O_5

λ (nm)	σ (cm^2)	λ (nm)	σ (cm^2)	λ (nm)	σ (cm^2)
206	6.6(-18)	246	4.3(-19)	286	7.8(-20)
208	5.9(-18)	248	3.8(-19)	288	7.1(-20)
210	5.2(-18)	250	3.5(-19)	290	6.3(-20)
212	4.4(-18)	252	3.0(-19)	292	5.7(-20)
214	3.7(-18)	254	2.72(-19)	294	4.9(-20)
216	3.0(-18)	256 .	2.55(-19)	296	4.4(-20)
218	2.48(-18)	258	2.33(-19)	298	3.8(-20)
220	2.06(-18)	260	2.12(-19)	300	3.2(-20)
222	1.71(-18)	262	1.97(-19)	302	2.7(-20)
224	1.41(-18)	264	1.86(-19)	304	2.4(-20)
226	1.23(-18)	266	1.7(-19)	306	2.1(-20)
228	1.06(-18)	268	1.64(-19)	308	1.8(-20)
230	9.3(-19)	270	1.52(-19)	310	1.5(-20)
232	8.4(-19)	272	1.42(-19)	320	7.5(-21)
234	7.5(-19)	274	1.31(-19)	330	4.0(-21)
236	6.9(-19)	276	1.2(-19)	340	2.7(-21)
238	6.3(-19)	278	1.15(-19)	350	1.8(-21)
240	5.7(-19)	280	1.07(-19)	360	1.0(-21)
242	5.3(-19)	282	9.9(-20)	370	4.7(-22)
244	4.7(-19)	284	8.9(-20)	380	1.3(-22)

Note: Numbers in parentheses signify powers of 10(e.g., 6.6(-18) = 6.6 x 10^{-18})

$H_2O_2 + h\nu \rightarrow OH + OH$
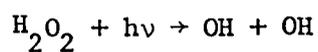
There are two measurements of the absorption cross sections of H_2O_2

vapor in the 300 nm region: Molina et al. (1977a) and Lin et al. (1978b).

The recommended values, listed in Table 10, are the mean of the two sets

of data.

Table 10.   Absorption Cross Sections of H_2O_2 Vapor

λ (nm)	$10^{20}\sigma$ (cm^2)
210	37.3
220	27.0
230	19.2
240	13.2
250	9.0
260	5.6
270	3.5
280	2.1
290	1.2
300	0.71
310	0.42
320	0.24
330	0.15
340	0.09
350	0.05

$HNO_3 + h\nu \rightarrow OH + NO_2$
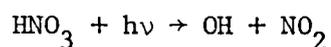
The recommended absorption cross sections, listed in Table 11, are taken from the review of Hudson and Kieffer (1975); the data are based on the work of Biaumé (1973) and of Johnston and Graham (1974). The quantum yield for production of OH and NO_2 is unity (Johnston and Graham, 1974).

Table 11.   Absorption Cross Sections of HNO_3 Vapor

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
190	1320	255	1.94
195	910	260	1.90
200	550	265	1.80
205	255	270	1.63
210	97.0	275	1.40
215	32.8	280	1.14
220	14.4	285	0.877
225	8.51	290	0.634
230	5.63	295	0.426
235	3.74	300	0.276
240	2.60	305	0.168
245	2.10	310	0.095
250	1.95	315	0.047
		320	0.018

$HO_2NO_2 + h\nu \rightarrow$ products
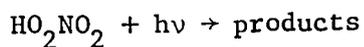
There are four studies of the UV spectrum of HO_2NO_2 vapor: Cox and Patrick (1979), Morel et al. (1980), Graham et al. (1978b) and Molina and Molina (1980). The latter two studies are the only ones covering the gas phase spectrum in the critical wavelength range for atmospheric photo-dissociation, that is, wavelengths longer than 290 nm. The recommended values listed in Table 12 are taken from the work of Molina and Molina (1980), which is the more direct study. The temperature dependence of the cross sections at these longer wavelengths and the identity of the photo-dissociation products remain to be determined.

Table 12.   Absorption Cross Sections of HO_2NO_2 Vapor

(nm)	$10^{20}\sigma$ $(cm)^2$			
	(a)*	(b)	(c)	(d)
190	1010		1610	
195	816	404	960	
200	563	434	640	435
205	367	420	430	382
210	241	378	290	289
215	164	298	200	232
220	120	220	154	164
225	95.2	163	123	121
230	80.8	120	99	97
235	69.8	93	82	86
240	59.1	76	68	74
245	49.7	65	58	61
250	41.8	54	51	52
255	35.1	44	45	40
260	27.8	30	40	34
265	22.4	<10	35	27
270	17.8		28	23
275	13.4		23	15
280	9.3		18	12
285	6.3		14	10
290	4.0		11	5
295	2.6		8.4	
300	1.6		6.2	
305	1.1		5.0	
310	0.7		4.2	
315	0.4		3.6	
320	0.3		3.0	
325	0.2		2.6	
330	0.1		2.2	

*   preferred value
(a) Molina and Molina (1980)
(b) Cox and Patrick (1979)

(c) Graham et al. (1978)
(d) Morel et al. (1980)

$$CH_2O + h\nu \rightarrow H + HCO \quad (\phi_1)$$
$$\rightarrow H_2 + CO \quad (\phi_2)$$
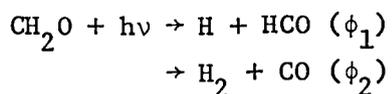
Moortgat and Warneck (1979) have reinvestigated the photolysis of CH_2O. Their results together with earlier studies have been reviewed by the CODATA Task Group on Chemical Kinetics (Baulch et al., 1980). The recommended values listed in Table 13 are taken from this review.

Table 13.   Absorption Cross Sections and Quantum Yields for the Photolysis of CH_2O

λ (nm)	$10^{20}\sigma$ (cm^2)	ϕ_1 (H + HCO)	ϕ_2 (H_2 + CO)
280	2.4	0.63	0.37
290	3.2	0.73	0.27
300	3.3	0.77	0.23
310	3.1	0.76	0.24
320	2.4	0.63	0.37
330	2.4	0.31	0.64
340	2.0	0	0.67
350	0.8	0	0.40
360	0.2	0	0.14

HCl + hν → H + Cl
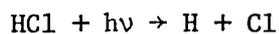
The absorptions cross sections of HCl, listed in Table 14, are taken from the review by Watson (1977); the values are based on the work of Inn (1975).

Table 14. Absorption Cross Sections of HCl Vapor

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
140	211	185	31.3
145	281	190	14.5
150	345	195	6.18
155	382	200	2.56
160	332	205	0.983
165	248	210	0.395
170	163	215	0.137
175	109	220	0.048
180	58.8		

$HOCl + h\nu \rightarrow OH + Cl$
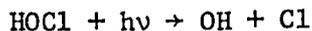
Knauth et al. (1979) have recently measured absorption cross sections of HOCl using essentially the same technique as Molina and Molina (1978) except for a higher temperature, which allowed them to obtain a more accurate value for the equilibrium constant Keq for the $H_2O - Cl_2O$ - HOCl system. The cross section values from Molina and Molina's measurements recalculated using the new Keq are in excellent agreement with the results of Knauth et al. The recommended values, taken from this later work, are presented in Table 15.

Molina et al. (1980), by monitoring directly OH radicals produced by laser photolysis of HOCl, obtain an absorption cross section value of $\sim 6 \times 10^{-20}$ cm^2 around 310 nm, again in excellent agreement with the data of Knauth et al. (1979).

In contrast, the theoretical predictions of Jaffe and Langhoff (1978) indicate negligible absorption at those wavelengths. The reason is not known, although it should be pointed out that no precedent exists to validate the theoretical approach for this particular type of problem.

Table 15. Absorption Cross Sections of HOCl

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
200	5.2	330	3.7
210	6.1	340	2.4
220	11.0	350	1.4
230	18.6	360	0.8
240	22.3	370	0.45
250	18.0	380	0.24
260	10.8	390	0.15
270	6.2	400	0.05
280	4.8	420	0.04
290	5.3		
300	6.1		
310	6.2		
320	5.0		

$ClONO_2 + h\nu \rightarrow$ products

The cross sections recommended in the NASA 1010 publication were based on measurements by Rowland, Spencer and Molina (1976). Molina and Molina (1979) carried out new measurements using essentially the same technique but under conditions of higher sensitivity (a longer absorption path), and as a function of temperature. Their room temperature values are ~15% lower than the earlier measurements. The recommended values, taken from the work of Molina and Molina (1979) are listed in Table 16.

The identity of the primary photolytic fragments has been investigated by two groups: Smith et al. (1977) report O + ClONO as the most likely products, using end product analysis and steady-state photolysis, whereas the results of Chang et al. (1979), who employed the "Very Low Pressure Photolysis" (VLPPh) technique, indicate that the products are Cl + NO_3. In view of the more direct nature of the VLPPh technique these later results are preferred.

Table 16. Absorption Cross Sections of $ClONO_2$

λ (nm)	10^{20} σ(cm)^2			λ (nm)	10^{20} σ(cm^2)		
	227K	243K	296K		227K	243K	296K
190	555	-	589	325	0.463	0.502	0.655
195	358	-	381	330	0.353	0.381	0.514
200	293	-	307	335	0.283	0.307	0.397
205	293	-	299	340	0.246	0.255	0.323
210	330	-	329	345	0.214	0.223	0.285
215	362	-	360	350	0.198	0.205	0.246
220	348	-	344	355	0.182	0.183	0.218
225	282	-	286	360	0.170	0.173	0.208
230	206	-	210	365	0.155	0.159	0.178
235	141	-	149	370	0.142	0.140	0.162
240	98.5	-	106	375	0.128	0.130	0.139
245	70.6	-	77.0	380	0.113	0.114	0.122
250	52.6	50.9	57.7	385	0.098	0.100	0.108
255	39.8	39.1	44.7	390	0.090	0.083	0.090
260	30.7	30.1	34.6	395	0.069	0.070	0.077
265	23.3	23.1	26.9	400	0.056	0.058	0.064
270	18.3	18.0	21.5	405	-	-	0.055
275	13.9	13.5	16.1	410	-	-	0.044
280	10.4	9.98	11.9	415	-	-	0.035
285	7.50	7.33	8.80	420	-	-	0.027
290	5.45	5.36	6.36	425	-	-	0.020
295	3.74	3.83	4.56	430	-	-	0.016
300	2.51	2.61	3.30	435	-	-	0.013
305	1.80	1.89	2.38	440	-	-	0.009
310	1.28	1.35	1.69	445	-	-	0.007
315	0.892	0.954	1.23	450	-	-	0.005
320	0.630	0.681	0.895				

Halocarbon Absorption Cross Sections and Quantum Yields

The primary process in the photodissociation of chlorinated hydrocarbons is well established: absorption of ultraviolet radiation in the lowest frequency band is interpreted as an $n-\sigma^*$ transition involving excitation to a repulsive electronic state (antibonding in C-Cl), which dissociates by breaking the carbon-chlorine bond (Majer and Simons, 1964). As expected, the chlorofluoromethanes--which are just a particular type of chlorinated hydrocarbons-- behave in this fashion (Sandorfy, 1976). At shorter wavelengths, two halogen atoms can be released simultaneously in the primary process. The quantum yield for photodissociation of chlorinated hydrocarbons is, thus, expected to be unity; the studies which show specifically that this is the case for CF_2Cl_2, $CFCl_3$ and CCl_4 have been reviewed by Watson (1977).

The recommended absorption cross sections for CCl_4, CCl_3F, CCl_2F_2, $CHClF_2$ and CH_3Cl, listed in Tables 17 through 21, remain unchanged from the NASA 1010 evaluation. Several authors have remeasured these cross sections--e.g., Hubrich et al. (1977); Hubrich and Stuhl (1980); Vanlaethem-Meurée et al. (1978a,b); Green and Wayne (1976-1977)--and their results are in good agreement with the values listed in the tables, so that for atmospheric modeling purposes it was not considered necessary to change the recommendations. These authors have also studied absorption cross sections and their temperature dependency for other halocarbons not listed here; among them, $CHCl_3$, CH_2Cl_2, CH_2ClF, $CClF_3$, CCl_2FCClF_2, $CClF_2CClF_2$, CF_3CClF_2, CF_3CH_2Cl, CH_3CClF_2 and CH_3CH_2Cl.

$CCl_4 + h\nu \rightarrow$ products

The recommended absorption cross sections of CCl_4, taken from the review by Watson (1977), are listed in Table 17. The values are based on the work of Rowland and Molina (1975) and of Robbins et al. (1975).

Table 17. Absorption Cross Sections of CCl_4

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
174	995	206	56.5
176	1007	208	52.8
178	976	210	47.3
180	772	212	39.6
182	589	214	33.4
184	450	216	27.6
186	318	218	22.1
188	218	220	17.0
190	142	222	12.8
192	98.9	224	9.5
194	73.3	226	7.1
196	67.6	228	5.6
198	65.1	230	4.11
200	64.1	232	3.05
202	61.4	234	2.24
204	60.1	236	1.52
		238	1.25

$CCL_3F + h\nu \rightarrow$ products

The preferred absorption cross sections, listed in Table 18, are the mean of the values reported by Chou et al. (1977), Robbins and Stolarski (1976) and Bass and Ledford (1978). The cross sections are temperature dependent (see, for example, Chou et al. 1977), but this effect is relatively small at the stratospherically important wavelengths, i.e., near the 200 nm "window".

Table 18. Absorption Cross Sections of CCl_3F

λ (nm)	$10^{20}\sigma(cm^2)$
186.0	243.0
187.8	217.0
189.6	186.0
191.4	159.0
193.2	133.0
195.1	111.0
197.0	90.3
199.0	73.0
201.0	57.3
203.0	45.2
205.1	33.3
207.3	23.9
209.4	16.8
211.6	11.5
213.9	7.6
216.2	5.0
218.6	3.1
221.0	2.0
223.5	1.2
226.0	0.8

$CCl_2F_2 + h\nu \rightarrow$ products
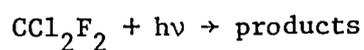
The preferred absorption cross sections listed in Table 19, are the mean of

the values reported by Chou et al. (1977b), Robbins and Stolarski (1976), and Bass

and Ledford (1978). For simplicity, the recommended low temperature values

are given by the expression provided by Chou et al. (1977b), which is listed

in Table 19.

Table 19. Absorption Cross Sections of CCl_2F_2

λ (nm)	$10^{20}\sigma_{296}$ (cm^2)
186.0	106.0
187.8	85.4
189.6	64.6
191.4	48.7
193.2	35.3
195.1	24.5
197.0	16.6
199.0	10.8
201.0	6.87
203.0	4.36
205.1	2.59
207.3	1.50
209.4	0.89
211.6	0.51
213.9	0.29
216.2	0.17
218.6	0.095
221.0	0.05
223.5	<0.05
226.0	<0.05

$$\sigma_T = \sigma_{296}\exp[3.6 \times 10^{-4}(\lambda-184.9)(T-296)]$$

Where: σ_{296} : cross section at 296K

λ : nm

T : temperature, Kelvin

$CHClF_2 + h\nu \rightarrow$ products
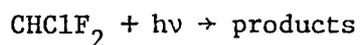
The preferred absorption cross sections, listed in Table 20 and taken from the review by Watson (1977), are the mean of the values reported by Robbins and Stolarski (1976) and Chou et al. (1976).

Table 20. Absorption Cross Sections of $CHClF_2$

λ (nm)	$10^{20}\sigma(cm^2)$
174	5.94
176	4.06
178	2.85
180	1.99
182	1.30
184	0.825
186	0.476
188	0.339
190	0.235
192	0.157
194	0.100
196	0.070
198	0.039
200	0.026
202	0.022
204	0.013

$CH_3Cl + h\nu \rightarrow$ products
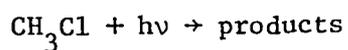
The preferred absorption cross sections, listed in Table 21 and taken from the review by Watson (1977), are based on the values reported by Robbins (1976).

Table 21. Absorption Cross Sections of CH_3Cl

| λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
174	110	198	2.60
176	93.3	200	1.69
178	77.3	202	1.09
180	63.5	204	0.718
182	46.5	206	0.476
184	34.7	208	0.302
186	25.3	210	0.191
188	18.0	212	0.116
190	12.5	214	0.089
192	8.76	216	0.047
194	5.61	218	0.036
196	3.80	220	0.023

$CH_3CCl_3 + h\nu \rightarrow$ products
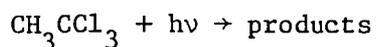
Table 22 lists the recent absorption cross section measurements of Vanlaethem-Meureé et al. (1979) and of Hubrich and Stuhl (1980). These latter authors corrected the results to account for the presence of a UV-absorbing stabilizer in their samples, a correction which might account for the rather large discrepancy in the two sets of measurements. The recommended values are taken from Vanlaethem-Meureé et al. (1979) (these authors report values at 210 K, 230 K, 250 K, 270 K and 295 K, every 2 nm, and in a separate table at wavelengths corresponding to the wavenumber intervals generally used in stratospheric photodissociation calculations). Table 22 lists the values at 210 K, 250 K and 295 K, every 5 nm; the odd wavelength values were computed by linear interpolation.

Table 22. Absorption Cross Sections of CH_3CCl_3

λ (nm)	$10^{20}\sigma (cm^2)$			
	(a)	(b)*		
	298K	295K	250K	210K
160	420			
165	411			
170	380			
175	394			
180	378			
185	290	265	265	265
190	210	192	192	192
195	162	129	129	129
200	101	81.0	81.0	81.0
205	56.3	46.0	44.0	42.3
210	38.7	24.0	21.6	19.8
215	20.2	10.3	8.67	7.47
220	10.3	4.15	3.42	2.90
225	4.36	1.76	1.28	0.97
230	1.75	0.700	0.470	0.330
235	0.614	0.282	0.152	0.088
240	0.211	0.102	0.048	0.024
245	0.088			
250	0.041			
255	0.016			

*   preferred values

(a)   Hubrich and Stuhl (1980)

(b)   Vanlaethem-Meurée et al. (1979)

$CCl_2O + h\nu \rightarrow$ products, $CClFO + h\nu \rightarrow$ products, and $CF_2O + h\nu \rightarrow$ products

Table 23 shows the absorption cross sections of CCl_2O (phosgene), $CClFO$, and CF_2O taken from the work of Chou et al. (1977a). The spectrum of CF_2O shows considerable structure; the values listed in Table 23 are averages over each 50-wavenumber interval. The spectrum of $CClFO$ shows less structure, and the CCl_2O spectrum is a continuum; its photodissociation quantum yield is unity (Calvert and Pitts, 1967).

Table 23. Absorption Cross Sections of CCl_2O, $CClFO$, and CF_2O

λ (nm)	$10^{20}\sigma\,(cm^2)$		
	CCl_2O	$CClFO$	CF_2O
184.9	204.0		4.7
186.0	189.0	15.6	5.5
187.8	137.0	14.0	5.2
189.6	117.0	13.4	4.5
191.4	93.7	12.9	4.0
193.2	69.7	12.7	3.3
195.1	52.5	12.5	2.8
197.0	41.0	12.4	2.3
199.0	31.8	12.3	1.9
201.0	25.0	12.0	1.4
203.0	20.4	11.7	1.1
205.1	16.9	11.2	0.86
207.3	15.1	10.5	0.65
209.4	13.4	9.7	0.48
211.6	12.2	9.0	0.36
213.9	11.7	7.9	0.26
216.2	11.6	6.9	0.21
218.6	11.9	5.8	0.15
221.0	12.3	4.8	0.12
223.5	12.8	4.0	0.10
226.0	13.2	3.1	0.08

$CH_3OOH + h\nu \rightarrow$ products
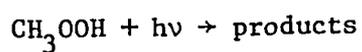
Molina and Arguello (1979) have measured the absorption cross sections of CH_3OOH vapor. Their results are listed in Table 24.

Table 24. Absorption Cross Sections of CH_3OOH

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
210	37.5	260	3.8	310	0.34
220	22.0	270	2.5	320	0.19
230	13.8	280	1.5	330	0.11
240	8.8	290	0.90	340	0.06
250	5.8	300	0.58	350	0.04

$BrONO_2 + h\nu \rightarrow$ products
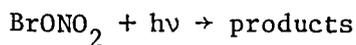
The bromine nitrate cross sections have been measured at room temperature
by Spencer and Rowland (1978) in the wavelength region 186-390 nm; their
results are given in Table 25. The photolysis products are not known.

Table 25. Absorption Cross Sections of $BrONO_2$

λ (nm)	σ (cm^2)	λ (nm)	σ (cm^2)
186	1.5(-17)	280	2.9(-19)
190	1.3(-17)	285	2.7(-19)
195	1.0(-17)	290	2.4(-19)
200	7.2(-18)	295	2.2(-19)
205	4.3(-18)	300	1.9(-19)
210	3.2(-18)	305	1.8(-19)
215	2.7(-18)	310	1.5(-19)
220	2.4(-18)	315	1.4(-19)
225	2.1(-18)	320	1.2(-19)
230	1.9(-18)	325	1.1(-19)
235	1.7(-18)	330	1.0(-19)
240	1.3(-18)	335	9.5(-20)
245	1.0(-18)	340	8.7(-20)
250	7.8(-19)	345	8.5(-20)
255	6.1(-19)	350	7.7(-20)
260	4.8(-19)	360	6.2(-20)
265	3.9(-19)	370	4.9(-20)
270	3.4(-19)	380	4.0(-20)
275	3.1(-19)	390	2.8(-20)

Note: Numbers in parentheses signify powers of
10 (e.g., 1.5(-17) = 1.5 x 10^{-17})

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